

Commentary

STREET LIGHTING

STREET lighting, other than by private individuals, was first introduced in 1405 and the first electric lighting scheme was installed almost exactly 80 years ago; it ran along the Thames Embankment and Holborn Viaduct. This is therefore perhaps as good a time as any to look around and take stock. Has street lighting kept pace with the rest of technological development?

The most suitable type of street lighting must depend on the use to which it is to be put, the capital cost, the running costs and the probable future needs of that particular piece of road. On traffic routes, as defined by the current British Standard, street lighting is intended to aid the motorist while on side roads it has been installed for the benefit of the pedestrian and to 'help prevent crime'. Little account seems to have been taken of the fact that, because of congestion on main routes, many side streets, still lit by dim gas lanterns, have become 'main traffic routes'.

Some modernization has been carried out over the last ten years, at a cost of £20 million¹, but only about one quarter of the 200,000 miles of road in Britain are illuminated at night, and of these at least half are still lit by gas. The latter seems a false economy for at least one council in the London area has found that the running costs and the repayments on the capital of new electric installations were smaller than the cost of running the existing gas installations; gas lanterns are exceedingly expensive to clean and maintain.

Four types of electric street lighting are in current use: yellow sodium lamps, high pressure mercury discharge lamps which give the characteristic 'blue' light, fluorescent lighting and, for side streets only, tungsten filament lamps similar to those used at home. Capital for new street lighting schemes is usually borrowed and repayed over a period of 20 years and, therefore, if we include this capital repayment in the running costs—power, replacements, cleaning and maintenance—the cost per lighting point of the different types of illumination on traffic routes is given below¹.

3×80W Fluorescent	140W Sodium	250W Mercury	400W Mercury	500W Tungsten
£15.5	£11.7	£13.6	£17.6	£18.9

The first three types of lamp gives about the same amount of light and it follows therefore that sodium and mercury discharge lamps are probably the best—the sodium may, in fact, be a little better than

the mercury—but in shopping areas it is often undesirable, from the ascetic point of view, to have either a blue or a yellow light and therefore fluorescent lamps are preferred. In fact if a much longer period than 20 years is considered, fluorescent lighting with its higher capital and lower running costs may well prove to have the advantage.

No one travelling along British roads, particularly after a journey abroad, can fail to notice the variegated colour scheme: yellow to blue to daylight and any other combination of these three. This seems one clear case for central planning. But the man who pays the piper should also call the tune and at present the local authorities do the paying and make the decisions. Many are enlightened and have installed systems that give more than the 18,000 lumens per 100 foot linear required by the British Standard² on traffic routes; a standard that is dated 1952 but was apparently compiled in 1937. (The government finances lighting on trunk roads by half the capital and running costs; the total annual cost of all street lighting is £12 million per annum³).

The introduction of improved street lighting does of course have a purpose, and a very important purpose at that: the reduction of accidents due to motor vehicles and, in metropolitan areas, the reduction of crime. (Residents and visitors to London will notice that most of the Soho area is still very inadequately lit by gas.) The Road Research Laboratory have carried out a series of tests on traffic routes before and after the installation of new lighting systems^{3,4} and have shown that accidents were reduced by about 30 per cent. There was a significantly greater reduction of accidents to pedestrians (about 45 per cent) than other accidents and no differences were observed between the three different types of discharge lighting. It is maintained that the saving in accident costs is 'more than sufficient to pay the increase in capital and running costs arising from the new installation'⁴.

There is obviously a great deal of opportunity for improving the illumination on British roads. A large proportion of the pre-war installations are due for modernization—only 5000 miles of new road lighting has been installed since the war⁵—and all of the 25,000 miles of gas are due for a rapid change of face in the near future. There is certainly a strong case for investment in brighter—and safer—roads.

¹ BERRY, G. J. *Instn Municipal Engrs* (1959) 86, No. 2, 58

² *British Standard CP1004*: Part 1: 1952

³ CHRISTIE, A. W. and MOORE, R. L. *Public Lighting* (1958) 23, 242

⁴ TANNER, J. C. *Light & Lighting* (1958) 51, 353

SOME AUSTRALIAN RESEARCH ON WOOL

II—Wool Textile Processing

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Australia as one of the largest producers of wool in the world has, needless to say, been very concerned with improving the quality of its product in the face of growing competition from synthetic fibres. The processes which have been developed for cleaning, mothproofing, shrinkproofing and permanent creasing of wool are important technological advances in the processing of wool.

THE AUSTRALIAN textile research programme is concerned with overcoming the disadvantages of wool as a textile fibre, devising improved methods of processing and developing novel properties in fabrics made from wool. With this in view, the fundamental chemistry and the structure of wool fibres have been extensively investigated*.

The processing research to date has been concentrated on the worsted system which absorbs about 80 per cent of the Australian clip. The investigations have been concerned in the main part with the earlier stages of processing going from greasy wool to top. One of the reasons for this approach is the fact that later stages from top to yarn have been very well covered in the United Kingdom with developments such as the Raper Autoleveller and the Ambler Superdraft. The present article outlines some of the practical developments resulting from the research which has been in progress now for ten years mainly at the Geelong laboratories (see Figure 1).

Sheep Branding Fluids

It is customary for wool growers to mark their sheep for identification and for many years products such as Stockholm tar and similar materials were used for this purpose. These preparations were not removed from the wool when scoured and persisted through subsequent stages of manufacture, appearing as black specks in the final fabric. To remove them at the final stage, manufacturers had to adopt tedious processes such as solvent treatment of the material which was quite an expensive operation. It was estimated that an extra annual expense of £2 million was involved due to the use of these harmful products.

The Australian research on this problem has concentrated on developing something which will

stay on the sheep in the field for a year and then be removed without any difficulty in subsequent normal processing. This has led to the development of a product called SI-RO-MARK branding fluid. The fluid has passed satisfactorily through field and mill trials and is now widely used by Australian wool growers; about 90 per cent of branded sheep in Australia carry this mark and its use has greatly alleviated the branding fluid problem. SI-RO-MARK branding fluid is a water in oil emulsion of lanolin, rosin, stearic acid, and solvents to which suitable pigments have been added. The C.S.I.R.O. has registered the name as a certification mark and private manufacturers have been licensed to market it; at present 26 approved firms are already marketing the fluid in Australia.

Solvent Degreasing

A weakness of wool compared with many other fibres is that the raw material as produced by the sheep contains a high percentage of impurities in addition to the fibre itself. These impurities consist of natural secretions such as lanolin and suint, together with extraneous materials such as sand, grass, seed and burr. To remove these impurities, the fleece is usually washed in aqueous detergent solutions which tend to felt the fibres. They then have to be torn apart in the later processing stages, such as carding, which results in fibre breakage and the production of waste.

A solvent degreasing process for raw wool has been developed as an alternative to the conventional soap-soda aqueous scouring system. In this process, the wool is carried on a perforated conveyor under jets of white spirit, followed by jets of cold water which remove much of the residual white spirit from the wool and any water soluble impurities (Figure 2). The white spirit-water mixture from the second stage is centrifuged to recover the white spirit; the latter is

* See Part I—Structure and Chemistry of Wool by F. G. LENNOX published in the March issue of RESEARCH.



Figure 1. General view of the Geelong Wool Research Laboratories, Division of Textile Industry, C.S.I.R.O.

also recovered from the first stage by first centrifuging, in order to remove solids, followed by vacuum distillation. In this way, a high recovery of lanolin is achieved. A commercial unit based on this principle has now been in operation in one large Australian mill for the past year where it is operating satisfactorily on a three shift basis.

Solvent degreased wool is less felted than wool scoured in the normal way in soap and soda solutions. Experiments on processing solvent degreased wool show that less fibre breakage occurs in carding and combing. This can have considerable economical advantages and it is possible to process solvent degreased wool differently from normally scoured wool. In particular, higher production rates in carding can be obtained because as the wool is less felted it can be put through the carding machines much more quickly. Plans are now in hand for extending this method to the United Kingdom and it is hoped to have a full scale demonstration plant erected in Bradford in 1959. This plant will be available for mills who wish to have their wool processed on it for comparison with the product obtained by the normal scouring techniques.

Carbonizing

The removal of burr and seed from scoured wool has been investigated with a view of minimizing fibre damage. The usual method for removing vegetable material in high concentrations is to treat with an aqueous solution of sulphuric acid and to follow this with a baking treatment which carbonizes the burr so that it can be crushed and removed from the wool.

This method often damages the wool, it weakens fibres and causes losses during processing.

Some fundamental research on the protective action of surface active agents against acid attack on proteins has led to a simple method of protecting wool from acid carbonizing. A non-ionic surface active agent is added to the acid used in the carbonizing and this protects the wool from acid damage. Australian carbonizers are now using this technique.

Worsted Combing

Until recently, there has been but little alteration in the equipment used for wool processing since the nineteenth century. Research in the United Kingdom has led to some outstanding developments such as the Raper Autoleveller and the Ambler Superdraft, which considerably reduce the number of machines required to produce a worsted yarn from a combed top. There has, however, been little advance of a similar nature in the earlier stages of worsted carding and combing and Australian research therefore concentrated on these stages. A recent outcome has been the development of an autocontrol unit for the Noble comb.

In studies on Noble combing, it was found that the production rate from a Noble comb, which depends on manual setting, fluctuates tremendously during processing even though the machine operator was under the impression that the output was being maintained at a constant rate. The C.S.I.R.O. comb control unit overcomes fluctuations which cannot be eliminated by manual control. It consists of a



Figure 2. Pilot plant for degreasing wool

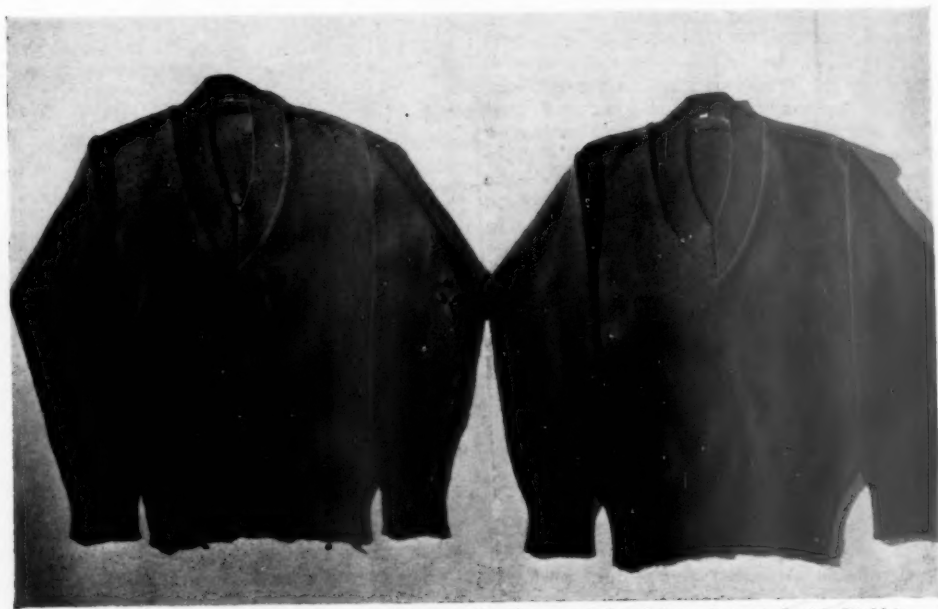


Figure 3. Two garments exposed to moth larvae—(LEFT) untreated and (RIGHT) treated with Dieldrin

mechanical measuring device which assesses the output of wool sliver at regular intervals and then through an electric servo-system controls the feed knives to the comb to compensate for any variations. Using this equipment, it has been possible to reduce production variations which originally were of the order of twenty per cent to less than five per cent.

A prototype machine has been constructed and was recently demonstrated to the Australian industry. It is planned to have an initial quantity of these units commercially available and they should be in operation in Australian mills early in 1959.

Mothproofing

The mothproofing of wool has in the past been studied by research groups in several countries. In Switzerland and Germany, products were developed which could be applied to the wool from the dye bath and combined with the fibre similarly to a dye but, instead of colouring the wool, rendered it toxic to moth larvae. These compounds have given very satisfactory results in commercial processing but mothproofing has not become widely adopted mainly on account of the cost of treatment. With a view to developing cheaper methods, research in Australia has followed several lines. One finding was that wool could be protected from moth larval attack if certain types of anionic surface active agents were added to the acid dye bath. These compounds were exhausted on to the wool in a similar manner to those mentioned above and protected it from subsequent attack. However, it was found that they did not possess sufficient fastness to light and washing for the method to have general application. Other lines were therefore studied and this work has led to a convenient and cheap method for producing a satisfactory result.

In this method, the wool is treated, usually in the last wet processing operation, with an emulsion of Dieldrin using 0.05 per cent of pure compound on the weight of wool (see Figure 3). The Dieldrin usually exhausts from the emulsion on to the fibre during treatment. An unexpected finding was that the result is fast to dry cleaning even though Dieldrin is soluble in the white spirit used by dry cleaners. On the other hand, if Dieldrin is applied from a white spirit solution instead of an emulsion, the effect is not fast to dry cleaning.

It was at first thought that Dieldrin may be combining with certain side chains in the wool when treated from emulsion but recent research has shown that this is not so. It appears that the swelling of the wool fibre in aqueous solution permits a small quantity of Dieldrin to penetrate the fibre. This small amount, which is sufficient to protect the wool

from moth larval attack, resists removal by the organic solvents used in dry cleaning. Although 0.05 per cent of Dieldrin is applied to the wool, this is considerably more than is in fact required to prevent attack; for moth larvae, only 0.0005 per cent of the weight of wool is required whilst for carpet beetles 0.005 per cent is the minimum quantity.

The treatment of wool with Dieldrin has been widely adopted by the major mills in Australia and it is now also being used in other countries including the United States, Britain and Japan.

Shrinkproofing

Research on shrinkproofing has followed two major lines. The first is that by using synthetic resins to more or less spot-weld the fibres in a fabric, the fibres are unable to move during washing. This type of treatment has previously been studied in the United States, in Britain and in Europe, and for some time now melamine resins have been used to shrinkproof wool. In Australia, resin treatments for shrinkproofing have been concerned mainly with polyamide materials such as methoxy methyl nylon and with proteins such as casein (see Figure 4).

Some years ago, a shrinkproofing method was developed which depended on the application of methoxy methyl nylon from alcoholic solution followed by acid hydrolysis of the deposit on the wool to nylon. The method has been used commercially on hosiery but its adoption has been limited due to the high cost of treatment. Another approach using casein followed by after treatment with formaldehyde has also produced satisfactory results on the laboratory scale.

In the course of this work, it was found that all resin treatments need some form of pretreatment of the wool so that shrinkproofing can be achieved with quantities of polymer insufficient to alter the handle of the fabric. For instance, if the wool is extracted with alcohol before resin treatment, then polymer contents of the order of one per cent of the weight of wool are sufficient. If this extraction is not carried out, much higher amounts of polymer are required—of the order of five to ten per cent—which affect the handle of the wool. The reason for this is now being investigated. It appears that there is a small amount of alcohol soluble material remaining on the wool fibre and related chemically to the original wool wax which is responsible for this difference.

In the meantime, chemical methods of shrinkproofing depending on modification of the scale surface of the fibre are being investigated. Experiments are in progress analysing the scales from

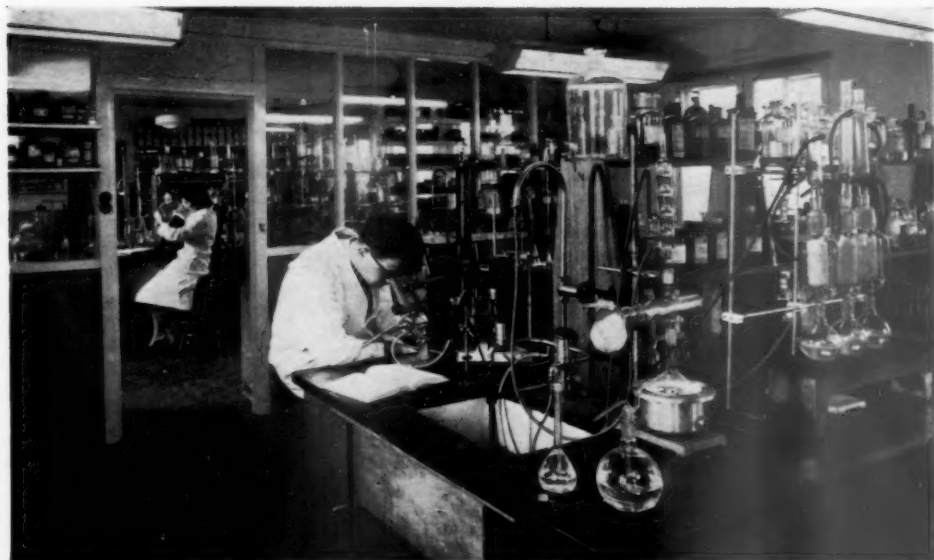


Figure 4. A general view of the chemical laboratory at Geelong which carries out research on shrinkproofing

individual fibres shrinkproofed by various reagents to obtain a fuller knowledge of their action. In addition, research on alternative shrinkproofing reagents is being undertaken.

Permanent Pleating and Creasing

The SI-RO-SET process for putting permanent creases or pleats into wool garments is the result of fundamental research. In the SI-RO-SET process, wool is treated with a solution of ammonium thioglycollate containing a wetting agent followed by steaming; in the case of trousers, on a Hoffman press and for skirts treatment in a steam box or autoclave. The reagent reacts with some of the disulphide bonds in the wool fibre and the water present breaks hydrogen bonds during the heating treatment. Thus there are three essentials for the process: ammonium thioglycollate, water, and heat. All of these are necessary and need to be present for satisfactory results.

In commercial operation, a two per cent solution of thioglycollic acid in the form of the ammonium salt is applied to the goods usually by a spray gun or mechanized spray unit. An essential requirement is that after spraying the goods must also contain water to the extent of 40 per cent of the weight to be treated. If insufficient water is present, then the results will be unsatisfactory. The sprayed garments are then pressed or pleated for the required time on the appropriate equipment.

The SI-RO-SET process has been in commercial operation in Australia for the past year. During that period, half a million pairs of trousers have been treated as well as large quantities of pleated skirts. The method has now been extended to other countries through cooperation with the International Wool Secretariat in London and the Wool Bureau in New York. Arrangements have been made in overseas countries for certain approved firms to supply the SI-RO-SET concentrate to users; the solution then has to be diluted with water before application.

It is considered that the SI-RO-SET process will help wool in providing an answer to one of the questions posed by the synthetic fibres where permanent pleating and creasing were first promoted as new effects. Fabrics treated by the SI-RO-SET process have creases or pleats which withstand normal wear and wetting but, in general, treated garments should be dry cleaned and not washed.

We have therefore been able to confer on a natural product three of the advantages of man-made fibres—mothproofness, resistance to shrinking and permanent pleating or creasing—while retaining the 'warmth' and elasticity of the wool fibre. Experiments are now in progress in which the SI-RO-SET treatment is associated with a shrinkproofing treatment on the same fabric. In this way it will be possible to obtain wash and wear effects which were hitherto unobtainable on pure wool garments.

SOME OPTICAL CHARACTERISTICS OF SEMICONDUCTORS

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This is the seventh article in the series on semiconductors; the next article will deal with zone refining. The optical absorption of semiconductors can give a wealth of information about the electronic structure of perfect crystals, the properties of impurity atoms and other imperfections, and the behaviour of current carriers. A number of optical phenomena are described, together with sufficient discussion of the electronic structure of semiconductors to show what kind of information can be derived from the measurements.

ALMOST all the important electrical properties of a solid depend upon the distribution of energy among its population of electrons, and also on the way in which the electrons interact with the lattice which contains them. The object of this article is to discuss some of the optical properties of crystals, and to show what kind of information these observations can give about the behaviour of the electrons in a semiconductor.

Perhaps the most elementary property of a solid is its colour. We may describe a crystal as being transparent, or coloured, or lustrous, or metallic as the case may be. This visual appearance is determined by two physical properties of the crystal, its transmission of visible light and its reflectivity. Even a qualitative description of this kind already gives some information about the nature of the solid; thus a transparent crystal is probably an insulator because there are no electrons available for conduction which require less than the quantum energy of blue light, three electron volts, to release them. A coloured crystal may be an insulator, as is the case with copper sulphate, or it may be a semiconductor such as cadmium sulphide. A lustrous or metallic appearance denotes a high reflectivity, and this is usually due to a combination of high refractive index and absorption coefficient, which is characteristic of semiconductors and metals.

A great deal more information can be derived if the absorption of light is measured as a function of wavelength. The interesting spectrum extends beyond the visible into the far infra-red, and in some cases also towards shorter wavelengths in the ultra-violet. To understand the importance of the absorption coefficient it is necessary to consider what happens when a quantum of light is absorbed by a crystal. A photon carries energy but negligible momentum; when it is absorbed conservation requires the total energy of the crystal to increase,

but its momentum to remain unchanged. There are a number of ways in which the crystal can take up the photon energy, and we shall discuss some of the most important; each gives information of a particular kind about the electronic structure of the crystal.

In principle any process of absorption of light has an inverse in which light is emitted. Such emission of light can only occur if the crystal is excited by some means so that energy is available for release by radiation. We shall describe a few effects which are relevant to semiconductors, but luminescence is for the most part outside the scope of this article.

Comparatively recently the influence of magnetic fields on the optical properties of semiconductors has been intensively studied. Rather high fields are needed, and some of the phenomena are only observable at very low temperatures. The effects which are of interest are analogous to the Zeeman effect in atomic spectra, and the fine structure in the absorption is an important new source of information. We conclude with a discussion of this topic, on account of its great contemporary interest.

Band-to-Band Transitions

The energy of an electron in free space is related to its momentum p by the simple expression

$$E = p^2/2m,$$

where m is the electron mass. This no longer holds for an electron in a crystal because it is moving in the field of the atomic lattice and all the other electrons. Calculations show that the permissible electron energies are grouped into bands, and that there are ranges of energy which are disallowed. Figure 1 shows two cases of importance in semiconductors, both are simplified by considering only electrons with momenta in one direction in the

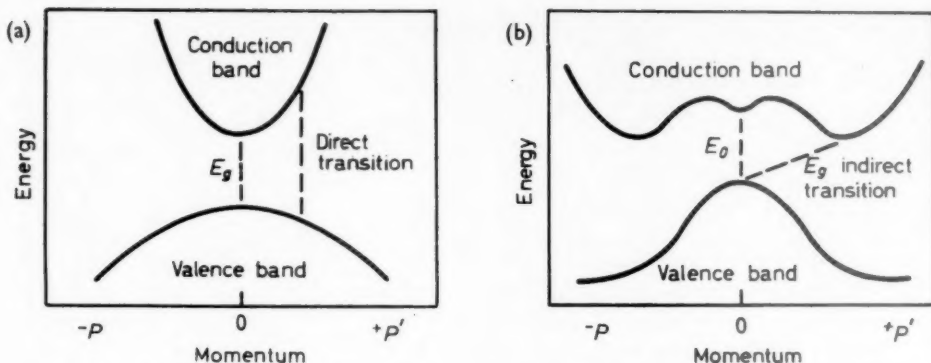


Figure 1. Energy bands in (a) a simple semiconductor and (b) with the conduction minimum not at zero momentum

crystal. Figure 1a shows a simple semiconductor in which the minimum energy of an electron in the conduction band has zero momentum. Figure 1b shows the case in which the lowest energy level in the conduction band does not have zero momentum.

Measurement of the absorption coefficient of a semiconductor is one of the principal methods used to find out the way in which the electron energy varies with momentum. Normally the valence band in a semiconductor is almost fully occupied by electrons and the conduction band is almost empty; absorption of light can cause electrons to be excited from the valence band into the conduction band. Transitions of this kind generally involve a change in both the energy and momentum of an electron, but for transitions shown on the diagram by vertical lines the momentum change is zero.

Considering Figure 1a, it is easy to see that a semiconductor with a simple energy band scheme will be unable to absorb light of wavelengths such that the quantum energy is less than E_g , the forbidden energy gap. E_g is thus the threshold for absorption, and photons with energy exceeding E_g are able to excite electrons with no change of momentum; such transitions are called direct, or vertical. The situation is quite different in a semiconductor with a band structure as shown in Figure 1b, because the minimum energy difference between the bands is associated with a change of momentum, and a photon is unable to supply this.

There is, however, an alternative source from which momentum can be derived; this is the vibration of the crystal lattice caused by the thermal motion of its atoms. If an electron is able to absorb simultaneously the energy of a photon and the momentum of a lattice vibration it is possible for indirect, or non-vertical, transitions to occur. (There is simul-

taneously a small exchange of energy Δ between the electron and the lattice, which may be either positive or negative.) This is exactly what is observed in the absorption spectra of germanium and silicon¹, which are known to have non-zero momentum at the conduction band minimum. Indirect transitions are much less probable than direct transitions, and consequently the long wavelength absorption appears as quite a weak 'tail' beyond the absorption limit for vertical excitation.

An idealized absorption spectrum of a semiconductor with direct and indirect transitions is shown in Figure 2; the diagram is simplified by the omission of detailed structure in the absorption tail due to transitions which will not be discussed here. The absorption tail has two components, corresponding to the absorption or emission of the lattice vibration energy Δ , and these have long wavelength cut-offs at $E_g - \Delta$ and $E_g + \Delta$ respectively. The following information can be derived from the absorption spectrum.

(i) The energy difference between the top of the valence band and the centre of the conduction band, for which the momentum change is zero; this is E_0 .

(ii) The minimum energy difference between the valence band and the conduction band; this is the thermal energy gap E_g observed in electrical measurements.

(iii) The value of the momentum in the conduction band for which the energy is minimum; this can be deduced if it is known what momentum of the lattice corresponds to a vibrational energy Δ .

Free Carrier Absorption

So far we have considered only transitions which raise an electron from the valence band into the conduction band. Such a transition results in the

creation of a pair of current carriers, one additional electron in the conduction band, and one positive hole in the valence band. There are, however, always a few free electron and hole pairs present in a semiconductor due to thermal excitation; in an impure semiconductor there may also be a large number of carriers, either holes or electrons, due to thermal ionization of impurity centres.

Free carriers are able to absorb infra-red radiation by making transitions within one band. A simple theory predicts that the absorption due to free carriers increases proportionately to the square of the wavelength; this is unlike band-to-band absorption which decreases with increasing wavelength. Free electrons in the conduction band obey the λ^2 law quite well, and it is possible to deduce the effective electron mass from this information. (An electron in a semiconductor behaves as if it had a mass different from the free space value. The effective mass m^* , which can be measured experimentally in a number of ways, is of great importance in the theory of semiconductors.)

Absorption by free holes within the valence band also occurs in *p*-type semiconductors. These show additional absorption beyond the limit for band-to-band transitions, which differs from the free electron case in *n*-type semiconductors by having a spectrum consisting of several broad bands superposed on the λ^2 dependence. Figure 3 shows qualitatively the form of the free hole absorption, such as is observed in *p*-type germanium or gallium arsenide². Structure

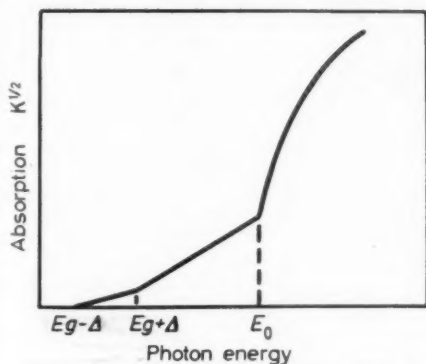


Figure 2. Absorption spectrum of band-to-band transitions

in the free carrier absorption spectrum cannot be explained by a model of the valence band like that shown in Figure 1b; theory requires the valence band to contain carriers of several discrete energies for each value of momentum, so that a better model is that of several overlapping sub-bands. The

structure in the free hole absorption arises from transitions between sub-levels of the valence band.

Analysis of this absorption is a powerful means of investigating the valence band structure, and it is able to give information both about the relative

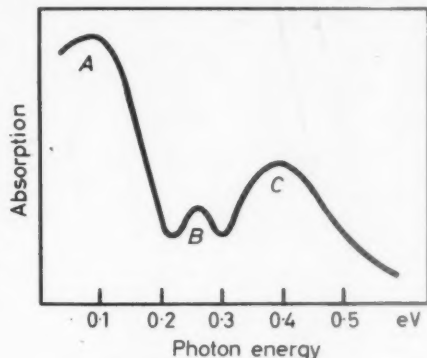


Figure 3. Free hole absorption in germanium

energies of the sub-bands, and also the effective masses of the holes. Figure 4 shows the three sub-bands in germanium, and the assignment of transitions corresponding to the absorption maxima in Figure 3.

Absorption by Impurities

At room temperature the impurity centres in an *n*-type semiconductor, such as germanium containing arsenic, are mostly ionized and a corresponding number of free electrons are to be found in the conduction band. If now the temperature is decreased the electrons will ultimately all be frozen out by capture at the positively charged centres, and neutral impurities will result. In exactly the same way positive holes can be frozen out in a *p*-type semiconductor. During this process the free carrier absorption disappears, to be replaced by a quite different infra-red absorption spectrum due to the impurity atoms.

The temperature at which the carriers are frozen out depends on the ionization energy of the impurity centres; if it is as low as 0.01 eV—group III acceptors or group V donors in germanium—it is necessary to go to liquid helium temperatures to observe the effect. The corresponding impurity absorption is in the very far infra-red at about 100μ wavelength. Not all impurity ionization energies are so small; copper, nickel and iron in germanium and silicon for example have ionization energies 0.3 to 0.5 eV. Even higher values are observed in large gap semiconductors like zinc sulphide and diamond.

A simple theory of impurity centres treats the neutral atom of an impurity like a hydrogen atom embedded in a medium of dielectric constant equal to that of the semiconductor. The absorption of

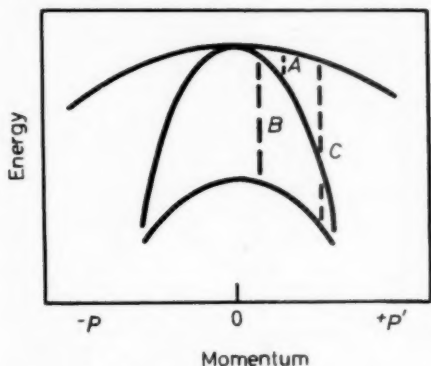


Figure 4. Valence band of germanium showing assignment of absorption maxima in Figure 3

such a centre can be shown to consist of a series of sharp lines leading up to a series limit at the impurity ionization, and continuous absorption at higher photon energies. Observation of the series limit is a method by which impurity ionization energies can be measured.

Figure 5 shows the absorption of aluminium acceptor centres in silicon at 4°K. The spectrum is more complex than that deduced from the simple hydrogen atom model, but almost all the principal features can be explained by a more detailed theory which takes into account the band structure of the semiconductor as well as its dielectric constant³. The remaining discrepancies are fundamental to the theory of the electronic structure of solids, and their elucidation is a topic of great contemporary interest.

Recombination Radiation

Two of the three absorption processes which we have considered cause an increase in the number of free charge carriers. The principle of detailed balancing requires the inverse process of recombination of carriers with emission of radiation to occur also, and there is a well defined average lifetime of a free carrier before it decays by this process. For simplicity we will consider only recombination of hole-electron pairs, which is the inverse of band-to-band transitions.

Since the conductivity of a semiconductor is proportional to the concentration of carriers, one way of measuring the rate of recombination is to observe the rate of decay of photoconductivity

after irradiation. When this is done it is invariably the case that the number of quanta emitted is less than the reduction in the number of pairs of carriers. The explanation is that radiative recombination is in competition with other modes of recombination that are non-radiative. For example, non-radiative recombination occurs at crystalline defects such as deep lying impurity centres and dislocations. Observation of recombination radiation is thus a means of acquiring information about processes which reduce the lifetime of carriers in crystals.

A necessary condition for recombination radiation to occur is that the number of holes and electrons should exceed the value at thermal equilibrium. Disequilibrium in carrier concentration can be caused in other ways than by absorption of light. When a rectifying *p-n* junction is biased in the forward direction minority carriers are injected into the bulk of the semiconductor, and the concentration of hole-electron pairs in the vicinity of the junction exceeds equilibrium. Rectifying junctions in silicon carbide show intense emission of visible light due to this cause. A similar phenomenon in gallium phosphide has been attributed to minority carrier injection at *p-n-p* junctions caused by the segregation of impurities at grain boundaries⁴.

A very beautiful example of recombination radiation has been observed at reverse biased *p-n*

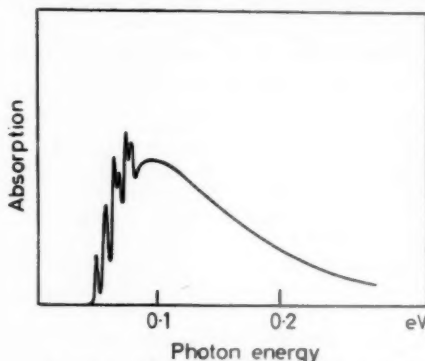


Figure 5. Absorption by aluminium acceptor centres in silicon

junctions in silicon. In this case there is no disequilibrium of carriers in the range of stable operation. When the applied voltage is sufficiently high for avalanche breakdown to occur carriers are injected into the junction, and recombination radiation is emitted. The light is not, however, uniformly distributed over the area of the junction, but forms a pattern of spots which are often arranged in a network of lines, Figure 6. Com-

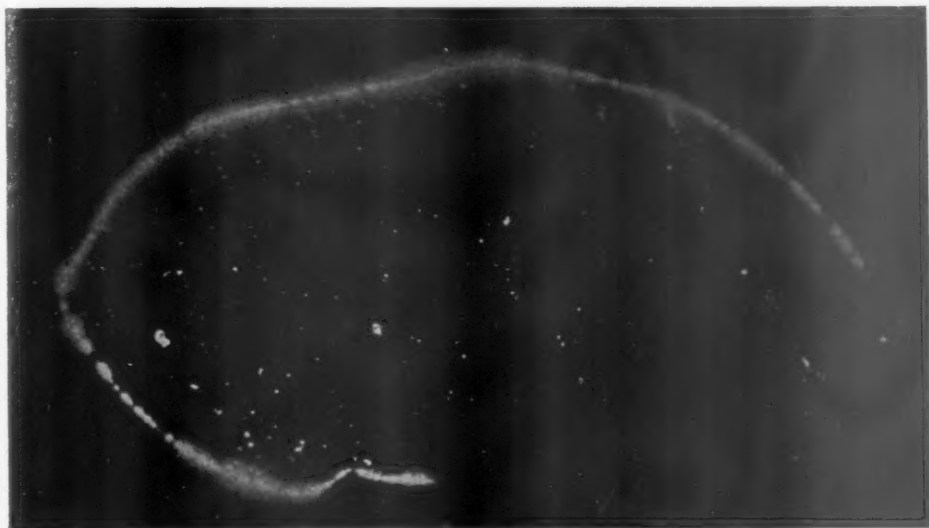


Figure 6. Luminescence at an n-p junction in silicon showing light concentrated at points where dislocations intersect the junction⁵ (by courtesy of The Editor of the Journal of Applied Physics)

parison of the light pattern with the distribution of etch pits definitely associates the light spots with points at which dislocation lines intersect the junction⁵. Evidence of this kind is of great value in understanding the part played by dislocations in the breakdown of semiconductor diodes.

Electroluminescence

Recombination radiation induced by electric fields is sometimes called electroluminescence. However there are other luminescent phenomena which accompany strong electric fields, and it is convenient to reserve the term electroluminescence for these. The most familiar electroluminescent semiconductor is zinc sulphide containing either copper or manganese impurity centres. Under the influence of sufficiently intense a.c. fields the phosphor exhibits brilliant luminescence, the colour being blue or green in ZnS(Cu) and yellow in ZnS(Mn).

The detailed mechanism of electroluminescence is still rather obscure, but it is generally accepted that there are four stages in the process. Firstly as the field increases electrons enter the conduction band from shallow donor levels; in the second stage these electrons are accelerated and may be multiplied by avalanching if the maximum field is close to breakdown. Thirdly a proportion of the electrons undergo collisions with the luminescent centres and transfer enough energy for the latter to be excited

or ionized. Finally the excited centres relax to the ground state with emission of a quantum of light characteristic of the impurity species.

Further discussion of electroluminescence would be out of place here because the problems it presents are electrical rather than optical in character. It is clear, however, that more information about the optical properties of impurity centres would enable the purely electrical difficulties of electroluminescence to be tackled with greater confidence.

Magneto-Optical Effects

It is well known that atomic spectra are modified when the emitting atoms are in a magnetic field. The Zeeman effect consists in the splitting of individual spectral lines into multiplets, and is one of the most powerful tools available for the investigation of atomic structure.

In a similar way the energy levels of electrons in a solid are modified in a magnetic field, and the resulting fine structure in the absorption spectra is becoming one of the best ways of studying the band structure of semiconductors. The Zeeman effect in semiconductors has only recently been observed, probably because it requires either rather high magnetic fields, or spectroscopy in the far infra-red at liquid helium temperatures. In spite of this a great variety of new effects have been reported in the last year or two.

An applied magnetic field affects bound electrons and free carriers in different ways. We have already remarked that a neutral impurity can be treated like

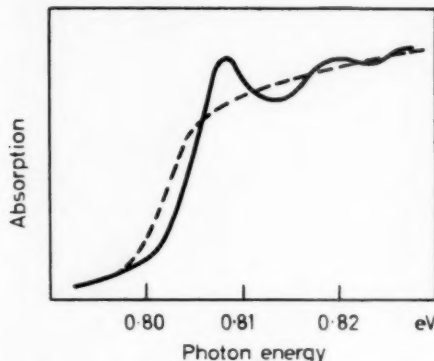


Figure 7. Oscillatory magneto-absorption in germanium at the direct transition edge

a hydrogen atom embedded in a dielectric medium, and this analogy also extends to the Zeeman effect. Although the theory is capable of much refinement the essential result is that the discrete energy levels of the impurity centre are split into multiplets, and the number of components and energy separations can be calculated. The infra-red absorption spectra of transitions between the ground state and excited states can thus be regarded as closely analogous to atomic Zeeman spectra.

The effect of a magnetic field on free carriers is more complicated. The energy-momentum curves that we used earlier to describe the band structure, Figure 1, are no longer meaningful. Instead the band is broken down into a set of sub-bands, known as Landau levels, equally spaced in energy. The separation between Landau levels in a magnetic field H is equal to $h\nu_c$, where

$$\nu_c = eH/2\pi m^*c$$

is known as the cyclotron frequency; h , e and c are Planck's constant, the electronic charge and the velocity of light. The name derives from the motion of charged particles in a cyclotron accelerator, where ions of mass M describe circular orbits in a plane

perpendicular to the magnetic field with a frequency of $eH/2\pi Mc$.

The subdivision of the band structure into Landau levels adds great complexity to all the absorption spectra which we have discussed above. It is not intended here to go into any detail of the magneto-optical effects, but it is worth mentioning two of the most important results. These are cyclotron resonance absorption, and the oscillatory magneto-absorption effect⁶.

Absorption by free carriers due to transitions between successive Landau levels is known as cyclotron resonance absorption. For fields of about one kilogauss ν_c is in the microwave region at a few centimetres wavelength. The first observations of cyclotron resonance were all microwave absorption experiments in resonant cavities. Some advantages can be obtained from using higher fields and observing the absorption by optical techniques in the infra-red. This method has been used at field strengths up to 300,000 gauss, and it is particularly suitable for the compound semiconductors indium antimonide InSb and indium arsenide InAs. With these materials, which have exceptionally small values of m^* , the absorption was observed at 12.7 μ wavelength.

The oscillatory magneto-absorption effect occurs in band-to-band transitions close to the absorption limits for direct and for indirect transitions. The oscillations arise from the various allowed transitions between the Landau levels in the valence band and the Landau levels in the conduction band. Selection rules apply for these in much the same way as for atomic spectra, and the resulting absorption is a complex of narrow bands. Figure 7 shows the oscillatory absorption in the direct transition of germanium.

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FROTH FLOTATION

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Froth flotation has proved to be a powerful tool for the separation both of natural materials and man-made chemical compounds. Although its application to the latter is still limited, the author believes that more research and development will yield good results. The paper is based on an entry in the 1958 Waverley Gold Medal Essay Competition.

WE ARE all familiar with metals like copper, zinc and lead, and perhaps aware that they are made from ores which occur in the crust of the earth. Few of us know in intimate detail the complex processes involved in their winning. One of the most important links in the chain between ore and metal is concentration of the ore. As mined, the ore may contain only one per cent of metal. The concentration step discards quartz and other barren constituents, and yields a product or concentrate with perhaps fifty per cent of metal, an appropriate material to feed into expensive smelting or electrolytic processes.

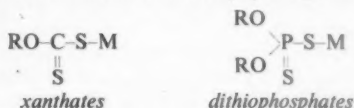
The metal often occurs in the ore as the sulphide, e.g., CuS, PbS, ZnS. These metal sulphides are heavier than impurities like quartz (SiO₂). In water, in accordance with Newton's law, large pieces of metal sulphide fall faster than equally large pieces of the unwanted materials, collectively called gangue. So in the nineteenth century, and before, a group of processes generically termed gravity concentration and based on this principle was elaborated, and proved quite effective for recovering metal sulphide particles from ores, provided these particles were larger than one-eighth of an inch. For fine grains, which fall in water only very slowly in accordance with Stokes' law, gravity concentration procedures were altogether unserviceable.

Then, at the turn of the century, to supplement the gravity concentration methods, there was invented the froth flotation process. It permitted the sulphides to be recovered efficiently even at sizes below one-hundredth of an inch. How does this process, by which nine-tenths of the ores of copper, zinc, and lead are now concentrated, work? It depends not at all on specific gravity differences between metal sulphide and gangue. It depends on differences, both natural and artificially created, in the wettability of the minerals which it is desired to separate.

Principle of Froth Flotation

If bubbles of air are passed through water containing small pieces of a hydrocarbon like paraffin wax, the particles attach themselves to the bubbles and ascend to the surface because they are hydrophobic (water-hating or air-avid); clean mineral surfaces are almost always hydrophilic (water-loving). When air bubbles are passed through an aqueous suspension of fine galena (PbS) and quartz (SiO₂) particles, neither mineral species attaches to the bubbles. The froth flotation invention was the discovery that by adding to the suspension in very small amount certain chemicals known as 'collector reagents', a valuable mineral like galena can be made hydrophobic. It will therefore attach itself to bubbles and can then be scraped off the top in a froth, while unwanted components like quartz remain hydrophilic and are discarded. In gravity concentration of coarse particles, galena sinks before quartz because it is heavier, but in froth flotation of fine particles, galena floats attached to air bubbles, because it has been made hydrophobic, while quartz (hydrophilic) remains in the water.

The chemical compounds which serve as collector reagents possess molecules of the type which chemists call amphipathic; at one end of the molecule is a polar group which ensures adsorption on the mineral surface, and at the other end a hydrocarbon group to cause attachment to the bubbles (see Figure 1). For metal sulphide flotation, sulphydic compounds are commonly employed, usually xanthates and dithiophosphates of the formulas shown below, where R is an aryl hydrocarbon group and M is an alkali metal in the sulphydic polar group.



Among collector reagents recently proposed are

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dithiophosphoryl chlorides¹, diglycol chloroformates with xanthates^{2,3}, 2-mercaptoimidazoles⁴, thiopyrimidines⁵, and substituted ureas⁶.

Small bubbles being better than large, a frother reagent such as pine oil or cresylic acid is usually

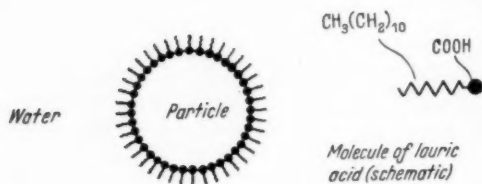


Figure 1. Molecules of lauric acid orientated on the surface of a mineral particle in water—the polar groups are absorbed on the surface of the mineral particle

employed, in addition to the collector reagent, which refines the bubble size. Among frothers recently suggested are substituted acyclic hydrocarbons of six to ten carbon atoms containing four to six alkoxy groups⁷, certain dioxane and alkoxy ester compounds⁸, and polypropylene glycols and phenyl monoethers of propylene⁹. Although J. LEJA and J. H. SCHULMAN¹⁰ from Langmuir trough experiments obtained evidence of reaction between xanthates and long chain alcohols at air-water interfaces and at solid-liquid surfaces, it is convenient in practice to consider that the main function of collectors is to alter the relative hydrophobicity of the minerals, and the primary purpose of frothers is to adjust the size of the bubbles.

Native Metals and Near Metals

The first practical froth flotation plant began to recover galena (PbS) at Broken Hill, New South Wales, in 1902. Later the ore mined in this region contained sphalerite (ZnS) in addition to galena, and an elegant variant of the process, called differential flotation, was developed to produce separate concentrates of lead sulphide and zinc sulphide from the same ore. In present day practice, after grinding to liberate the minerals, galena is first floated with sodium ethyl xanthate as collector and a eucalyptus oil frother¹¹. The suspension or 'pulp' is then agitated with a little copper sulphate, which forms a very thin layer of copper sulphide on the surface of the sphalerite (Figure 2); the zinc sulphide can then be floated, vicariously, with the same xanthate and a cresylic acid frother. By lime addition, the circuits are maintained alkaline, to prevent pyrite (FeS₂) from floating and contaminating the lead and zinc concentrates. If, finally, the pulp is made acid,

pyrite can be floated with a xanthate collector¹². (It may be of interest to mention that the rugosity of the surface of pyrite markedly affects its ease of flotation¹³.)

Another place where a similar process is used is at Laurium in Greece where over 2000 years ago a great silver mine existed. Today sulphide concentrates of lead, zinc, and pyrite are being produced by differential flotation on the lines described in the preceding paragraph¹⁴. Like sphalerite, stibnite (Sb₂S₃) will float with sulphydric collectors if previously activated by copper sulphate. In Thuringia, Germany, a concentrate containing 60 per cent antimony is made with 80 per cent recovery from crude ore; the ore originally contains five per cent antimony¹⁵.

Since 1910 the flotation process has been applied to copper ores, particularly to the porphyry ores of America which only carry about one per cent of copper, as sulphide. A description of operations at a mill at Chuquicamata, Chile, which treats 30,000 tons of ore daily has recently been published: from an ore of 1.7 per cent copper, by floating with xanthate and dithiophosphate collectors and a pine oil frother more than 90 per cent of the copper is recovered in a concentrate assaying 40 per cent of the metal¹⁶. In the Lake Superior district native copper is recovered by flotation, and at Creighton, Ontario, nickel sulphide is floated with copper minerals¹⁷.

From Tsumeb, South West Africa, the first commercial flotation of germanium minerals was reported¹⁸ in 1954; conditioning is done with lime and sodium dichromate¹⁹.

The main stream of flotation development, very concisely traced above, has throughout been well supported by research. The schools of Wark and Sutherland in Australia, of Gaudin in Massachusetts, and of Hagihara and Sato in Japan may be mentioned in this connection.

Now we must turn to the diversification of the process, to its application in other directions. It will be helpful, as an aid to clear thinking, to adopt the model of a map, as shown in Figure 3. Then the main pillars of the structure, the flotation methods for native metals and for near-metals like metal sulphides, appear towards the north and after half a century of enthusiastic exploration the ground in the northern region may be regarded as fairly thoroughly charted.

Wax-like Materials

Beginning about 1925, exploration began towards the west of Figure 3 into the flotation of wax-like and naturally waterproof substances. For these a

collector reagent is not needed; only a frother is required.

The foremost representative of this class, by any standard whatever, is coal. Each year about four million tons of fine coal is now floated, an amount comparable with the quantity of a base metal concentrate such as galena²⁰. The separation of coal from shale in a flotation machine has been subjected to close scientific study²¹ and to a limited extent, addition of lime will prevent finely disseminated pyrite entering the froth with the coal²². Almost invariably, the frother used in coal flotation is a crude cresylic acid; for low rank coals the addition of kerosene or a fuel oil is beneficial²³. (Figures 4 and 5 show the froth flotation of coal in a single machine and in four machines in series.) Flotative power depends on molecular structure and polarity; for example, while aromatic amines do not float coal, diethylaminophenol is an excellent frother²⁴. Among monohydric alcohols and monocarboxylic acids the good frothers have five to ten carbon atoms²⁵, the optimum being eight.

Graphite floats with a frother alone; Scandinavian and American plants make recoveries over 90 per cent²⁶. Fossil resins are recovered by differential flotation from bituminous coals²⁷.

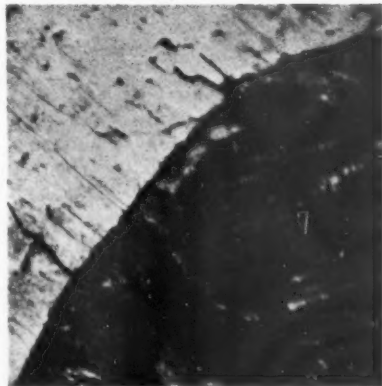


Figure 2. Sphalerite coated with copper sulphide as a result of treatment with copper sulphate (x 44)—reproduced from *Flotation* by A. M. GAUDIN (McGraw-Hill, 1932)

A fungus attacks the cereal known as rye, and converts some grains into black masses called ergot, a source of medicinal alkaloids. In Europe for many years it was the custom to allow chickens to eat the good grains, and afterwards to collect the remaining ergot. Now in Australia the black grains of ergot are separated from the good rye grains by flotation with a pure paraffin frother²⁸. In the same

way loose hulls and weed seeds are removed from peas and wheat by flotation with a pure liquid hydrocarbon²⁹.

Elemental sulphur is very difficult to wet with water. At Cody, Wyoming, an 87.5 per cent sulphur concentrate is made at 90 per cent recovery from an input containing 25 per cent sulphur, using kerosene and methyl isobutyl alcohol as frothers³⁰.

Finally we must mention a juxtaposition of unexpected ingredients which seems at first a paradox. Molybdenite (MoS_2) is a metal sulphide, but for many years it has been floated with a frother alone at Climax, Colorado³¹. The explanation is that this compound has a peculiar lattice structure. In consequence, unlike metals and the commoner metal sulphides it is a poor conductor of electricity, and is hydrophobic.

Earthy Materials

Exploration towards the east of Figure 3 into the concentration by flotation of earthy materials, only began to gain momentum about 1940. The key discovery was that a fatty acid collector, such as oleic acid or tall oil, would allow these substances to be floated away from quartz (SiO_2) and other siliceous compounds. The fatty acid also acts as a frother, but often pine oil or cresylic acid is added also to give closer control of bubble size.

The most prominent mineral of this group is fluorspar or fluorite (CaF_2); with the application of flotation a small production of 20,000 tons in 1940 has risen³² to 200,000 tons in 1957. The raw ore commonly contains equal amounts of fluorite and silica, about 45 per cent of each. Over 90 per cent of the fluorite is recovered in the froth, and over 99 per cent of the silica is discarded, to give a concentrate with more than 97.5 per cent of fluorite and less than one per cent of silica³³.

To make cement of good quality, calcareous and siliceous components in the kiln charge must be correctly balanced. Many natural mixtures are too high in silica and from these, with a tall oil collector, calcite and other carbonates may be floated, and a correct mixture made. At an American plant, 1000 tons of an 84 per cent calcium carbonate concentrate is produced daily from an input of 71 per cent carbonate³⁴. A plant in Finland treats 2000 tons of a low grade limestone containing only 65 per cent carbonate each day and recovers over 80 per cent of the calcite.

Drilling grade barytes with less than one per cent of silica is floated³⁵. For manufacturing pure barium salts an excellent raw material is the carbonate of barium known as witherite; this mineral is mined only at two places in the north of England. In

1953 witherite was shown to be amenable to concentration by froth flotation with oleic acid³⁶.

In former days only the coarse or 'pebble' portion of Florida phosphate rock could be sold. Now the fine portion is concentrated by flotation with tall oil and some fuel oil in alkaline circuit, and concentrates of apatite or fluorapatite constitute as high as 50 per cent of the output³⁷.

Exploitation of the iron ores of Michigan has been proceeding at an enormous pace, and inevitably the iron tenor of these oxides and carbonates has been falling. So the problem of finding an economic method for concentrating low grade iron ores has become increasingly urgent and in 1954 the first flotation plant for treating taconites and jaspers in Michigan was commissioned; using oleic acid as

collector, a product with 62 per cent iron and nine per cent silica is made³⁸. As will be seen in Figure 3, many other earthy materials besides those cursorily mentioned above are being won by froth flotation, using fatty acids as collector reagents. Exploration towards the east is only now developing in intensity and in this direction nothing like finality has been reached.

Siliceous Materials

In the flotation processes so far listed, the aim has been to float the valuable material, leaving siliceous substances behind in the pulp. On our map analogy, the separations described may be expressed in a sort of shorthand as N/S, W/S and E/S where the first letter indicates a wanted mineral reporting in the froth, and the second letter means quartz and other

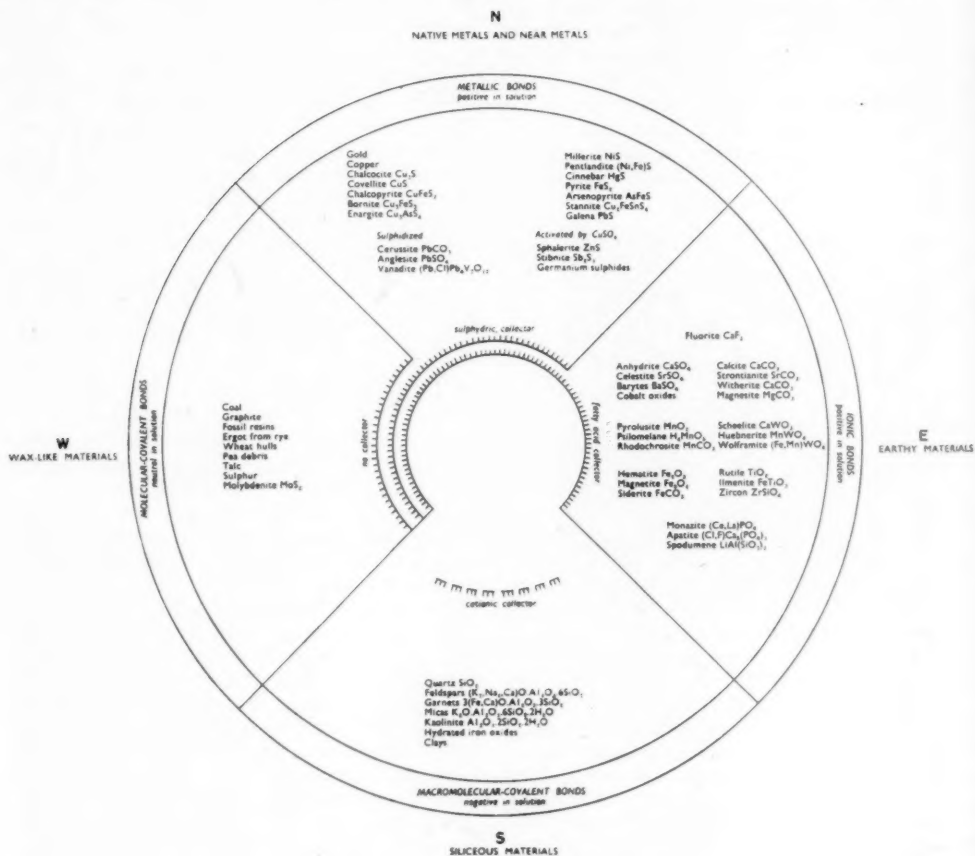


Figure 3. Froth flotation of natural materials

silicates remaining in the water. Sometimes the ore is rich and contains only a little siliceous gangue. Confronted with a choice between floating mineral or gangue, in these instances the most economical course would be to float the gangue—if that were possible.

From the electrochemical point of view, the collector reagents which make possible the flotation of native metals, near-metals, wax-like substances, and earthy materials—the xanthates, dithiophosphates, fatty acids, *etc*—are anionic. The question was therefore posed: would it be possible, by selecting a cationic reagent, to float quartz and other silicates, and leave the other minerals behind? This most sagacious suggestion was quickly followed up, and since about 1950 cationic reagents, usually long chain amines like laurylamine, have begun to be used for floating silicates.

Feldspar is floated in a strongly acid circuit by amine acetate³⁹, and silica is removed from a phosphate rock concentrate with tallow amines containing 16 to 18 carbon atoms⁴⁰.

The broad pattern of the application of flotation to natural materials may now be concisely pictured as follows. Considering *Figure 3*: to the north where we have native metals and near-metals, the ground is well charted already; to the west there are the wax-like and waterproof materials; to the east, exploration of the earthy substances, has been going on for some time and is being actively pursued; and to the south lies almost virgin country, and the possibilities for new discoveries are enormous.

Chemical Compounds

Our topographical analogy has now served its purpose, and we need another model. Let us inscribe the map corresponding to *Figure 3* on one side of a medal. If not only the highlights in the flotation of natural materials, already mentioned in this article, are inserted, but also the less outstanding, but established, processes, the map will show a wealth of descriptive detail and be full of interesting sidelights. Nevertheless, to east and west and especially towards the south there are still large unexplored areas, which will gradually be filled in.

One common feature is shared by all the flotation processes in the map—the raw material is natural, usually an ore dug out of the crust of the earth. These ores are the result of 1000 million years of metamorphosis by molten magmas and of attack by wind, water and ice. Now the modern scientist has armed himself with powerful solvents, high temperature furnaces, and other tools of research, which enable him to alter the composition of matter in a few minutes or hours as radically as did the slow

moving natural agencies over aeons of time. So it is not surprising that while materials number a few hundreds, the number of man-made chemical compounds already exceeds a million. Froth flotation



Figure 4. Single froth flotation machine floating coal—by courtesy of Denver Equipment Co.

tion has scored a success in application to natural products—will it not be of even greater value for separating the artificial or synthetic materials one from the other? To answer this question we turn over the medal. On its obverse, which bears the title 'chemical compounds', we find no intricate mass of lines, but only about a dozen faint scratches.

These traces are not spectacular, but they may be symptomatic of a great new development, and therefore for the aftermath important. It is not only possible, but likely, that they are the chink in the dam. In chemical engineering, flotation has only occasionally and not systematically and persistently been applied to the problems. As physicists and chemists become more aware of the power and economy of the flotation process, the enormity of its possibilities in the chemical field will begin to unfold.

The list of man-made substances at present floated is meagre, and follows.

(i) In the Western United States at Greater Butte about 10,000 tons of ore is mined daily; it contains about 1.1 per cent copper, whereof 0.2 per cent is present as copper oxide. By leaching with weak sulphuric acid the oxide is dissolved, and then by passing the solution over scrap iron, metallic copper is precipitated. The 'cement copper' is floated with a xanthoyl formate collector and a pine oil frother and a concentrate assaying 20 per cent copper is recovered from the mixture of copper, iron, iron oxide, graphite and other materials⁴¹.

(ii) The Kodak Company employs froth flotation to recover metallic silver from photographic residues⁴².

(iii) At the Ontario copper-nickel properties a matte consisting of sulphides of nickel, copper and iron is produced. Formerly, in the Orford process, this was carefully cooled so that it divided into a bottom layer of the heavy nickel sulphide and a top layer containing the lighter copper sulphide and iron sulphide; the layers were smelted separately. In 1952 this process was superseded⁴³. The matte was cooled to give crystals of a desired size, ground to ensure liberation, and the copper sulphide and nickel sulphide were then separated by differential flotation⁴⁴.

(iv) Certain low grade ores contain sulphur grains only one to five microns in size. By passing in steam, these melt and agglomerate into 0.2 mm to 2 mm particles. Some of the coarse particles can simply be recovered by screening, and the remainder are floated with a pine oil-fuel oil frother⁴⁵.

(v) Sphalerite (ZnS) concentrates are roasted at Risdon, Tasmania, to convert them to oxide (ZnO) and sulphate (ZnSO₄), which are leached with acid to form electrolyte for zinc recovery. Although a temperature of 800° to 850°C is reached in the roaster, a little of the sphalerite is not oxidized. This exists in the insoluble residue (mostly silica) from acid leaching, and is separated by flotation and returned to the roaster⁴⁶.

(vi) Since cobalt would bring trouble if its concentration was allowed to increase in the electrolyte at Risdon, it is kept down to an innocuous level by adding nitroso-β-naphthol to the solution. The precipitate which forms contains cobalt nitroso-β-naphtholate, gypsum, and other substances. The cobalt compound is recovered from it by froth flotation without reagent addition, and is calcined to yield a saleable oxide, Co₃O₄, containing 65 per cent of cobalt⁴⁷.

(vi) In California natural brines occur containing potassium chloride and sodium chloride in about equal amount. For a long time the potassium

chloride, a valuable food for plants, was separated by complex techniques of fractional crystallization. Then valuable deposits were found in New Mexico, containing in about equal parts sylvite (potassium chloride) and halite (sodium chloride). An elegant method of froth flotation in a saturated solution was developed for their separation⁴⁸. With anionic collectors, particularly naphthenic acid or 2,4-dichlorophenoxyacetic acid, the halite may be floated, leaving only sylvite in suspension⁴⁹. Alternatively, with a long chain primary amine as collector, the sylvite may be floated away from the halite; the reaction products of kerosene with chlorine and ammonia, chlorinated aminated hydrocarbons of 6 to 21 carbon atoms, are valuable in this application⁵⁰. To mitigate the disastrous effect of excessive montmorillonitic slimes on the sylvite flotation, the polysaccharide mannogalacton, extracted from the guar bean, is useful⁵¹. In addition to four plants in America, a German plant is also floating potassium chloride from saturated brines; in all cases the product is 95 per cent pure⁵².

(vii) From alkaline brines at Searles Lake, California, which contain 0.05 per cent lithium oxide, a concentrate of dilithium-monosodium phosphate containing 20 per cent lithium oxide is produced by froth flotation⁵³.

(viii) Before spinning wool, wax must be washed from the fibres. The liquor obtained carries much dirt, 0.25 per cent of soap, and 0.5 to 5 per cent of wax. In Australia in 1953 a recovery of 80 per cent of the wax was achieved by flotation in a pilot plant. Now four plants float wool-wax in Australia⁵⁴, and one plant in New Zealand⁵⁵.

(ix) In petroleum refineries 75 to 95 per cent of the oil is recovered by flotation⁵⁶ from waste liquors.

(x) The flotation process also successfully treats laundry wastes, soap and fatty acid wastes, glue wastes and plaster board wastes⁵⁷. In these diverse applications, laurylamine hydrochloride and quaternary ammonium compounds have been used in addition to the more common anionic collectors. Laundry waste has been clarified by flotation sufficiently to permit its re-use, the aeration being through a porous ceramic cylinder⁵⁸.

(xi) Guanidine carbonate, made by double decomposition, can be separated from the sodium chloride produced simultaneously, by flotation with an appropriate collector⁵⁹.

Natural ores are very heterogeneous, both in the number of mineral species present and in size of crystal: in consequence, flotation can only recover 75 per cent to 95 per cent of the wanted constituent from these sources. In chemical preparations, in

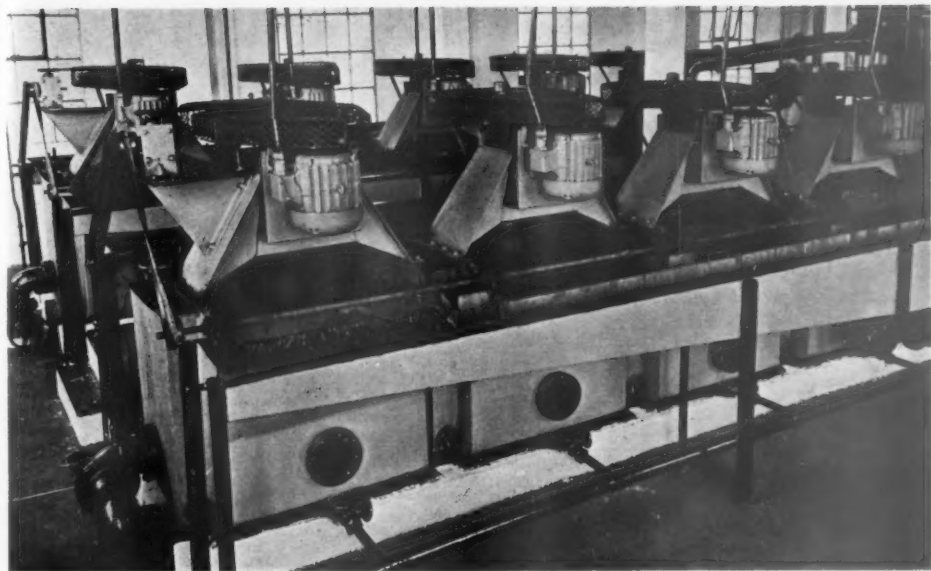


Figure 5. Four froth flotation machines in series used for floating coal—by courtesy of Denver Equipment Co.

contrast, a fairly uniform size of crystal may be made by accurate control of conditions, as in the sugar industry, and in general the product is not excessively contaminated by the presence of many other compounds. The production of two insoluble compounds by mixing solutions of two soluble materials is a rapid and inexpensive process: witness the manufacture of lithopone. In former days, when the pair of insoluble substances could not be easily separated, the method had limited utility; now that flotation is available, the situation is otherwise. If the chemist can arrange that one insoluble component has ionic bonding, and the other molecular, even the method of froth flotation already known will permit efficient separation.

Some Comments

The quantity of flotation reagent needed to cover ten per cent of the surface of one component with a monomolecular layer, which is enough to ensure attachment to air bubbles, is extremely small; about one part of collector is usually required for 10,000 parts of material. So the flotation process is far cheaper than the commoner unit operations of chemical engineering, such as fractional crystallization and distillation.

If a large company engaged in manufacturing a wide range of chemical products applied froth flota-

tion as a cheap separatory method, there are no limits to the results which might be achieved; if success were reached in laboratory studies, a whole series of practical and positive economies would immediately become possible in its production processes.

Fundamental research on froth flotation is one of the pressing needs of the present time. We must learn more about this process, not in the leisurely future, but at the earliest possible date. Much of our present knowledge is mere empiricism, and any processes founded on this insecure basis may fall into the chimerical class. Because flotation depends on reactions and physical changes in layers a few molecules thick between air, water, and solid, research work is beset with pitfalls and the problems often prove stubborn and eluctable. But as fundamental investigation will play an indispensable part in the extension of flotation, it will be appropriate to end this article by referring to two recent advances.

One of the thorniest problems is to trace the fate of the collector reagent. On which particles is it adsorbed, and how thick and continuous is the layer formed? By using radiotracer techniques—for example by incorporating radioactive phosphorus into the dithiophosphate molecule—and by measuring the radioactivity of the products after

flotation, a flood of light has been thrown on the problem during recent years. I. N. PLAKSIN and his collaborators in Moscow have now extended this technique and can even by an elaborate photographic method called automicroradiography determine which parts of a particle are covered by collector⁶⁰.

The cornerstone of the process is the mechanism of attachment of a particle to a bubble, and here time is a cardinal parameter. K. L. SUTHERLAND⁶¹ and W. PHILIPPOFF⁶² computed the time of contact needed, and L. F. EVANS⁶³ studied experimentally the thinning of the water film between a rotating silica disc and a captive bubble of air. The author and his colleagues tackled this problem at Cheltenham, using cinephotography at 2000 to 4000 frames a second, and in 1955 succeeded in measuring the actual contact time in dynamic systems in which both particle and bubble were moving, as they are in a practical flotation machine⁶⁴. For galena, pyrite, and coal particles, about 0.01 in. in diameter, contact times were respectively 1.3 to 2.7, 1.1 to 2.1, and 0.5 to 1.0 milliseconds. The probability of particle attachment was shown to be governed by the equation that per cent attachment is equal to $(k_1M - k_2MU)$ where M is particle mass, U is tangential velocity of the particle in relation to the bubble surface, and k_1 and k_2 are constants.

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EXTREME PRESSURE LUBRICANTS

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The development of lubricants which can withstand extremely high pressures and the high temperatures developed under these conditions is of relatively recent origin. Dr Pilpel reviews the properties of some of the materials which have been added to lubricating oils and the methods used to evaluate their effectiveness.

SOME measure of the novelty of extreme pressure lubricants may be gained by referring to a well-known book on lubricating oils¹, published in 1951. The relevant section states,

'A certain group of lubricants, the so called "extreme pressure lubricants" is effective only by chemical reaction with the surface, i.e., only the reaction product with the surface acts as the lubricant. These reaction products are inorganic and are formed at the spot and under the pressure and temperature resulting from incipient seizure. The systematic development of this group of lubricants and the theoretical understanding of their action is still too recent to permit profitable discussion at this time.'

And that, when it was written about ten years ago, summed up the position very fairly.

It was the development of hypoid gears, for use in motor cars² which disclosed one of the limitations of conventional lubricating oils and which stimulated the search for lubricants which could withstand the extremely high pressures which are developed in this type of gear. In fact it was the lack of suitable lubricants which was largely responsible for the slowness with which hypoids were generally introduced. They had appeared in the United States in the late 1920s and by 1937 about a dozen makes of car were using them. It was not, however, until after the end of the war that hypoid rear axles became common. In the 1950 motor show in London half the makes exhibited had hypoid rear axles but by 1954 this figure had risen to over 70 per cent.

The first successful lubricants for hypoid gears consisted of mineral oils to which had been added small amounts of lead soaps and compounds containing active sulphur. In the late 1930s additives containing active chlorine, and active phosphorus were introduced, both for hypoid lubrication and as lubricants in the cutting and drawing of metals where similarly high pressures and temperatures are encountered. During the war the use of all types of extreme pressure lubricants was considerably expanded, and a review of the patents taken out in this period shows that, in one form or another,

almost every element in the periodic table has been claimed to have extreme pressure characteristics.

Much of the early work was essentially empirical. But in the last ten or fifteen years a very much clearer understanding has been gained on the way in which extreme pressure lubricants act.

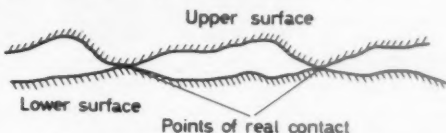


Figure 1. Contact between metallic surfaces (schematic)

General Characteristics

Extreme pressure lubricants must satisfy three basic requirements. First, their load bearing capacity at the highest pressures encountered must be great enough to prevent direct contact between the metallic surfaces concerned. When metallic surfaces, which are moving past each other under high pressure, come into direct contact very high temperatures develop at the local points of 'real' contact³ (Figure 1). This leads to melting and the formation of local welds. If sufficient of these are produced the surfaces seize up. Thus the first requirement is that the extreme pressure lubricant should possess good anti-welding properties.

The second requirement is that it should be capable of reducing friction and wear by the normal mechanisms of fluid and boundary lubrication⁴⁻⁵ so that it will be effective not only at extremely high pressures, but also over the whole range of working conditions. Fluid lubrication depends primarily on the viscosity characteristics of the lubricant, boundary lubrication on the presence in it of surface active materials which are selectively adsorbed on metallic surfaces. It follows that an extreme pressure lubricant should contain a mineral oil to provide fluid lubrication, a suitable soap or other additive to provide boundary lubrication and the special

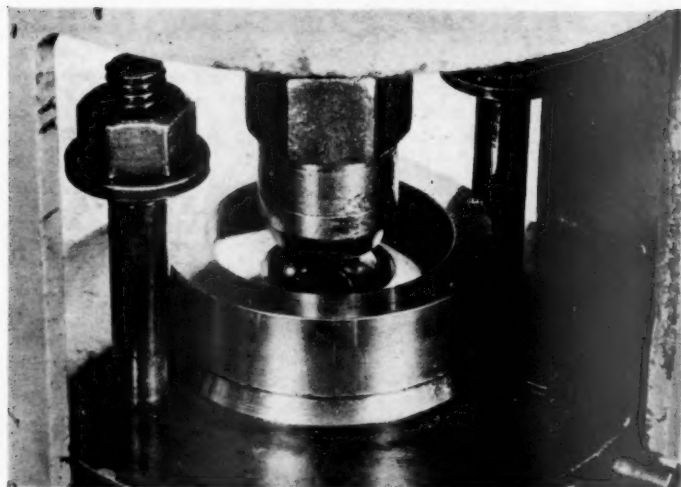


Figure 2. Four-ball machine—from *Lubrication of Bearings* by F. T. Barwell (London: Butterworths Scientific Publications, 1956)

additive or additives which provide lubrication only when conditions of extreme pressure obtain.

The third requirement is of a more general nature. The lubricant must be stable, both physically and chemically, it must be compatible with other lubricants, while on standing or storage it must not cause corrosion.

The use of the terms 'extreme pressure lubricants' and 'extreme pressure additives'—the latter referring to the particular ingredients in the lubricants responsible for their ability to carry extreme loads—is, to some extent, misleading. For it has now become clear that the mechanism of extreme pressure lubrication is essentially controlled by the temperatures rather than by the pressures at incipient seizure. At high temperatures these additives react chemically with the metallic surfaces concerned and it is the products of the reaction which subsequently provide the lubrication. Pressure alone will not initiate reaction. Temperature, however, will and extreme pressure additives have in fact been used in lubricants for high temperature operation when the pressures involved were normal.

A more realistic name, perhaps, would be extreme temperature lubricants/additives. However, some distinction would then have to be made between the present materials which act as a result of a chemical reaction and ordinary high temperature lubricants, *e.g.*, silicones⁶, fluorinated esters⁷, and inhibited oils⁸, which are effective simply because they can withstand high temperatures without decomposing.

Very broadly extreme pressure additives may be divided into three main types containing

- (i) reactive sulphur compounds,
- (ii) reactive chlorine or other halogens, and
- (iii) phosphorus compounds.

A typical extreme pressure lubricant may contain more than one type of additive but it is convenient at this stage to consider the three types separately.

Additives Containing Sulphur

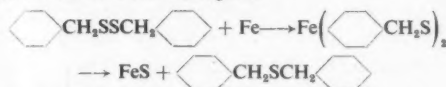
The essential requirement is that, by one mechanism or another, the sulphur should react with the metallic surface. Some metals, *e.g.*, platinum and silver are resistant to such attack and cannot be employed under extreme pressure conditions⁹. But even using metals which are susceptible to attack such as iron, copper, tin, cadmium, bronze, brass, *etc.*, it does not follow that all sulphur containing compounds are necessarily capable of providing extreme pressure lubrication. Indeed extreme pressure activity appears to be the exception rather than the rule and relatively few of the sulphur compounds out of all those that are known are effective. Some examples are given below.



Considering first the sulphides, it seems that in general di- and polysulphides are effective while monosulphides are ineffective⁹. The so called

'sulphurized oils'¹⁰ which are widely used in extreme pressure lubrication are complex materials but certainly contain polysulphides.

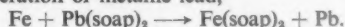
Detailed examination^{11,12} of the surface of copper lubricated with di- or polysulphide under extreme pressure conditions has clearly established that a layer of copper sulphide is formed on the surface of the metal. Similar experiments¹³ have shown that when steel is used a layer of iron sulphide is formed. W. DAVEY⁹ has proposed a reaction mechanism for the particular case of dibenzyl disulphide on steel. The first step involves the formation of iron mercaptide



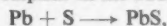
which then breaks down to form iron sulphide and dibenzyl sulphide. A similar mechanism satisfactorily explains the action of polysulphides on steel, although it may be noted that for these D. TURNBULL *et al.*¹⁴ have postulated an alternative mechanism.

In many cases sulphur compounds for extreme pressure lubrication are used in conjunction with lead soaps such as the naphthenate or stearate. By

studying such systems it has been shown^{15,16} that on surfaces of steel metal interchange occurs with the liberation of metallic lead,



This reacts with sulphur in the additive to form lead sulphide



which under load is plastic¹⁷ at 700°C. It thus provides a lubricating film at a temperature well below that at which steel surfaces would melt and seize up. The mechanism has been confirmed by the detection of the iron soap in solution in the oil, and a similar mechanism applies when a copper soap is used instead of a lead soap.

There is an advantage in using sulphur compounds in conjunction with metallic soaps, rather than on their own for although a sulphide layer has good anti-weld properties, it is found that the coefficient of friction of a sulphide film never falls below about 0.5 unless a soap is also present³. The soap appears to spread in a layer above the sulphide acting as a boundary lubricant until its melting point is reached. In this way, not only is there a reduction in surface damage and wear, but the coefficient of friction between the surfaces is also reduced.

Another group of sulphur compounds which is effective in extreme pressure lubrication is that in

Table 1. Typical phosphorus additives

Compound	Formula	Type
Tri- <i>o</i> -cresyl phosphite	$(\text{C}_6\text{H}_4\text{CH}_3)_3\text{PO}_3$	aromatic phosphite
Tri- <i>o</i> -cresyl phosphate	$(\text{C}_6\text{H}_4\text{CH}_3)_3\text{PO}_4$	Aromatic phosphate
Dibutyl dithiophosphite	$(\text{C}_4\text{H}_9)_2\text{HPS}_2\text{O}$	aliphatic thiophosphite
Sodium diphenyl dithiophosphate	$(\text{C}_6\text{H}_5)_2\text{PS}_2\text{O}_2\text{Na}$	aromatic thiophosphate

Table 2. Effect of phosphating on gear performance²⁵

Treatment	Rating treated/untreated	Rating after 100 h treated/untreated
(i) Untreated	1.0	1.0
(ii) Ferrous and manganese phosphate (deep, high temperature treatment)	2.1	2.0
(iii) Ferrous and zinc phosphate (shallow, medium temperature treatment)	1.5—1.5	1.2—1.5
(iv) Treatment (iii) prolonged	1.7	1.2
(v) Ferrous and zinc phosphate (low temperature, shallow treatment)	1.6	1.1

which the sulphur is present in the form of a thiocyanate -CNS radical. As an example one can mention dithiocyanostearic acid, prepared from oleic acid and thiocyanogen. Such compounds are more selective than the sulphides; they operate on iron and steel surfaces but not on copper, cadmium, tin, etc. It is believed that their action is due to the formation of a film of ferric thiocyanate on the surface of the iron or steel. This view is supported by the results of frictional experiments on steel surfaces on which thin films of ferric thiocyanate had been deposited by direct exposure to ethereal solutions of thiocyanogen⁹.

Additives Containing Halogens

The extreme pressure activity of compounds containing chlorine, like those containing sulphur, depends both on the nature of the compound and on the nature of the surface involved.

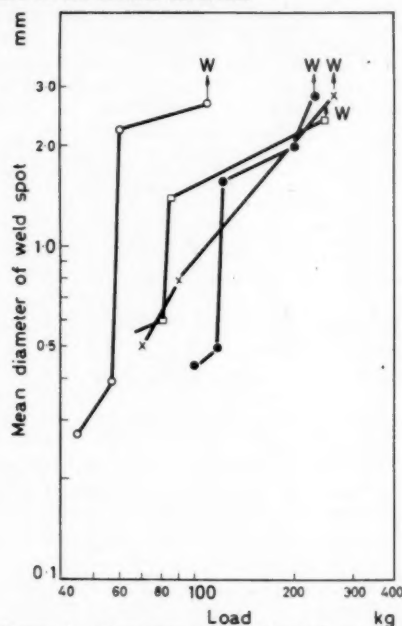
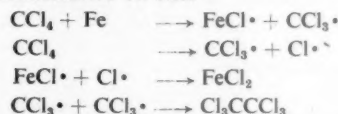


Figure 3. Wear tests on the four-ball machine²⁷ using a base oil and additives. \circ is I.S.55; \times is 1% dibenzyl disulphide I.S.65; \bullet is 1% di-n-butyl dithiodiacetate I.S.115; \square is 1.5% di-n-butyl dithiodisobutyrate I.S.85. (W denotes weld and I.S. incipient seizure)

Compounds like, for example, octadecyl chloride $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{Cl}$, and *p*-dichlorobenzene are not effective since the chlorine atoms they contain are not labile. Stearoyl chloride $\text{CH}_3(\text{CH}_2)_{16}\text{COCl}$, benzyl chloride PhCH_2Cl , and benzotrichloride PhCCl_3 , on the other hand, are effective for their

chlorine is liberated under extreme pressure conditions and reacts chemically with metallic surfaces. It has been shown^{3,18} that the products of reaction are the appropriate metal chlorides and the following reaction scheme is postulated by W. DAVEY¹⁸ for carbon tetrachloride on steel



Ferrous chloride, which forms the lubricating film, has a relatively low melting point, 670° to 674°C, and shears readily. This results³ in a low coefficient of friction, μ , of the order of 0.2 even at 300°C.

Various other reaction schemes have been postulated for the action of chlorine additives¹⁹, not only on steel, but also on surfaces of copper, cadmium, etc. But in all cases it appears that the chloride is formed. However, it is found that μ for copper and cadmium is about double that for steel which is presumably due to a difference in shear characteristics between a film of iron chloride and one of copper or cadmium chloride.

Lubrication by chlorine additives is adversely affected by the presence of moisture and this is ascribed to the formation of hydrochloric acid which causes corrosion and pitting of the surfaces. When active sulphur compounds are added to chlorine additives, on the other hand, extreme pressure activity may be enhanced. This is thought to be due to the formation of a mixed lubricating film of the sulphide and chloride of the metal. Similar results have been reported when sulphur additives are used in conjunction with bromine or iodine additives²⁰.

Although relatively little work has been done with these alternative halogens, it appears that on the whole bromine compounds are superior to chlorine compounds, but iodine compounds are inferior in their ability to provide extreme pressure lubrication.

Additives Containing Phosphorus

The third main group of additives capable of providing extreme pressure lubrication is that in which the element phosphorus is present. However, in comparison with the sulphur and halogen additives, very little systematic work has yet been done on phosphorus additives so that although some important findings have emerged, detailed mechanisms have not been worked out. At high temperatures many organic phosphorus compounds react with metals to form the metal phosphides and phosphide formation appears to be an essential condition for extreme pressure lubrication by these materials^{21,22}.

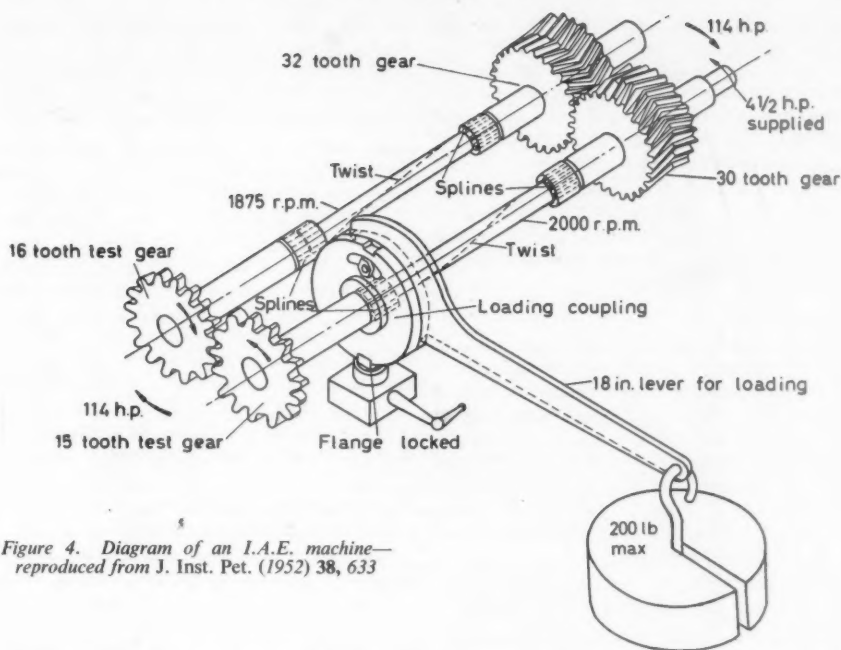


Figure 4. Diagram of an I.A.E. machine—reproduced from J. Inst. Pet. (1952) 38, 633

It has been shown²³ that in particular cases the layer of phosphide may react further with the metal substrate to produce a low melting eutectic of metal/metal phosphide. This is fluid under extreme pressure conditions and during sliding is wiped away to produce a smooth, polished surface. Thus lubrication by phosphorus additives may involve two somewhat different mechanisms, the first depending on the shear characteristics of a film of the appropriate metal phosphide, the second on the extent to which a phosphide/metal eutectic is formed and acts as a chemical polishing agent.

Some general conclusions have been reached on the connection between the chemical constitution of phosphorus additives and their efficiency in extreme pressure lubrication⁹. Considering the lubrication of steel, it is found that in general phosphites are superior to the corresponding phosphates (Table 1); aliphatic derivatives of phosphorus are superior to the corresponding aromatic derivatives; and thiophosphites and thiophosphates are superior to phosphites and phosphates. The efficiency of phosphites and phosphates is enhanced by blending them with sulphur additives and still further enhanced if reactive chlorine compounds are also incorporated. While the mechanisms of action of these compounds have not been worked out in detail, it will probably be found possible to explain

the experimental data in terms of phosphide films, mixed phosphide/sulphide (and halogen films) and phosphide/metal eutectics.

Methods of Testing

It is now appropriate to describe the methods that are used in practice for assessing the ability of different additives to provide extreme pressure lubrication. This may be done using a number of different test machines. Since, however, it is found that in evaluating a series of additives the different machines give different results, it is generally necessary to make tests with several different machines in order to arrive at a realistic idea of how a lubricant will stand up to service conditions.

The machines that are available include the four ball, the Almen, the Timken, the Falex, the S.A.E.²⁴, the I.A.E.²⁵ etc and for illustrative purposes the operation of two may be discussed.

The Four Ball Machine

The four ball machine^{24,26} consists of a 1/2 in. steel ball which is held in a chuck and rotated at constant speed (1500 rev/min) in the gap between three identical balls, clamped, and lubricated with the oil under test (Figure 2). The load is applied to the upper ball and this produces a frictional torque on the cup containing the lower balls.

As the load is increased the friction rises and this causes wear on the upper ball. After running for a standard time (one minute) the mean diameter of the wear spot is measured and a wear/load curve is then plotted, usually on log-log paper. From this the incipient seizure load, *I.S.*, the weld load, *W*, and the mean wear diameter of the spot at certain fixed loads can be read off. Some typical results are plotted in Figure 3 and it may be inferred that on this machine the curve for a good extreme pressure lubricant will lie to the right and below that of a poor one.

The I.A.E. Machine

The I.A.E. machine²⁵, on the other hand, has two pairs of gears torsionally loaded against each other, the two test gears being of coarse pitch with 15 and 16 teeth respectively (Figure 4). These are made either of case hardened two per cent nickel-molybdenum-manganese steel (B.S. En 34), or of 4.5 per cent nickel-chromium-manganese steel (B.S. En 36) and when running at their full distance apart ($3\frac{1}{2}$ in. from centre to centre), the gears work against each other at an angle of about 26 degrees.

The method of test is to run the machine for five minutes at a fixed speed, 2000, 4000, or 6000 rev/min, with constant load on the loading lever and to repeat with gradually increasing loads until the gears start to scuff. This is indicated by a decrease in running speed and the evolution of a cloud of oil vapour. By measuring the loads and

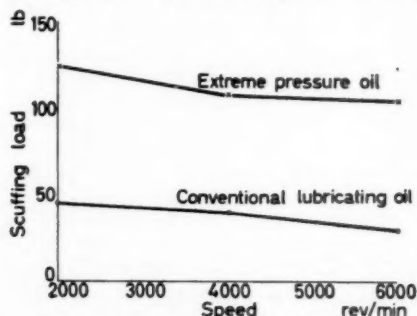


Figure 5. I.A.E. machine—scuffing load versus speed

speeds at which scuffing occurs for a series of lubricants, curves (see Figure 5) can be plotted, and these enable the relative merits of different additives under the conditions of the test to be assessed.

The use of these different test machines may be illustrated by reference to some recent work carried out by J. S. ELLIOTT and E. D. EDWARDS²⁷. A lubricant was required for a new type of steam

turbine in which the reduction gear was to operate under extreme pressure. Thus, not only had the lubricant to comply with the Admiralty Specification O.M.100 for steam turbine oils, but it also had to have a high load bearing capacity.

A number of additives was first examined for extreme pressure activity by dissolving each in a conventional lubricating oil and testing in either an S.A.E. or a four ball machine. Those which gave promising results were next dissolved in a conventional steam turbine oil, already containing oxidation and rust inhibitors, and the blends tested to see whether they still complied with specification O.M.100. Those which did were subjected to further testing on the David Brown disc machine, the Falex, I.A.E., Timken, and Ryder machines. On the basis of these tests an oil, L.H.38/52 was finally selected for full scale trials, and it has subsequently given very satisfactory performance in service.

This oil contains 1.5 per cent di-*n*-butyl trithiodiacetate as the extreme pressure reagent, 0.1 per cent benzothiazole disulphide—a deactivator to protect copper—and 0.1 per cent of an unspecified additive which, although not itself a copper protector, increases the protective action of the benzothiazole disulphide. Comparative data for L.H.38/52 and a conventional steam turbine oil are plotted in Figure 6 from which it is seen that the load bearing capacity of the former is substantially higher than that of the latter.

Conclusion

The growth of extreme pressure lubrication as a science has been very rapid since the outbreak of the last war. Every year the demand increases for machinery capable of running at higher speeds under increasingly exacting conditions, with lower frictional losses and less wear of moving parts.

In certain cases these requirements can be met by artifices. Thus solid lubricants, such as molybdenum disulphide, cadmium iodide *etc.*^{28,29} have good high temperature characteristics and can provide extreme pressure lubrication up to about 500°C for limited periods of time. However, the lubricating films are gradually wiped away and seizure of the surfaces then results.

Pretreatment of metallic parts with phosphates, sulphates and chlorides^{30,31} is another method whereby a lubricating film can be formed *in situ*. Phosphated steel, in particular, is now widely used in gears and some data²⁵ in Table 2 shows how such treatment increases the resistance of the gears to scuffing. But again the lubricating film is gradually wiped away and the gears need to be rephosphated. A recent development in chemical pretreatment

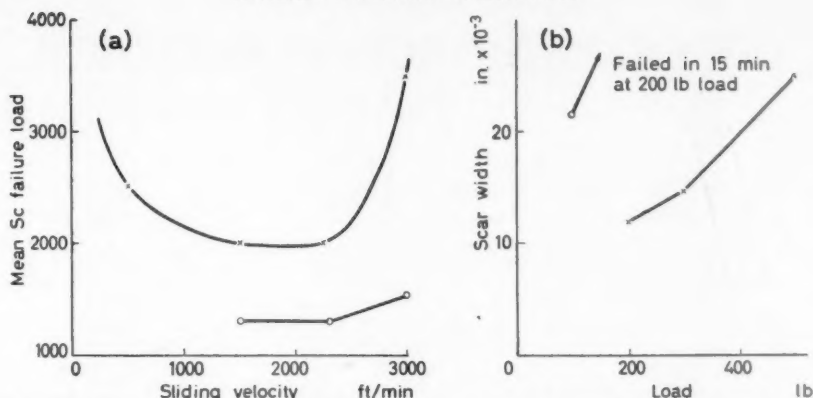


Figure 6. Comparative data for L.H.38/52 and a conventional steam turbine oil—(a) David Brown Dix machine tests and (b) Falex wear tests, (x represents L.H. 38/52 and o is conventional steam turbine oil). The disc material is B.S. En 36; diameter of discs is 8 in. (large) and 4 in. (small); speed of rotation of discs is 1800 rev/min (large) and 7200 rev/min. (small); sliding velocity is 3775 ft/min and the slide/roll ratio of the discs is 1.0 (large) and 0.5 (small). The oil temperature is about 70°C and the scuffing load 0.8 L/r where L is the load in lb/in of the length of line of contact and r the relative radius of curvature²⁷. The duration of test (b) was one hour at about 120°C

has been to fill the somewhat porous and fragile layer of phosphide, sulphide or chloride with polytetrafluoroethylene (P.T.F.E.) and the preliminary findings are encouraging^{32,33}. Not only is the life of the lubricating film extended, but the coefficient of friction is also substantially reduced.

It nevertheless remains a fact that for many applications, e.g., steam turbines, aero engines, hypoid gears, cutting tools and wire drawing equipment it is more satisfactory to employ fluid lubricants which can be circulated over the moving parts. As the extreme pressure layer is worn away it is continuously replaced by a fresh layer. At the same time the circulating fluid removes sludge and metallic fragments, and also acts as a coolant.

The number of compounds potentially available as extreme pressure additives is already very large and this number will grow as new compounds are synthesized and as increasing use is made of new alloys and of some of the less common metals for machine parts. A great deal of work, both practical and theoretical, remains to be done, offering an ideal opportunity for collaboration between industry and university research departments.

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THE USE OF RADIOACTIVE ISOTOPES

Part I—Engineering Applications

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Industry is progressively using more and more radioactive isotopes as these become readily available. This is the first of three articles to be published at monthly intervals which briefly survey some of the applications of isotopes; the first and the second, by Mr C. G. CLAYTON, deal with the engineering and metallurgical applications and the third, by Dr H. J. M. BOWEN, discusses some applications in agriculture.

DURING the past ten years there has been increasing application of radioactive isotopes in engineering and in the scientific and technological aspects of metallurgy. The object of this paper is to review some of the different principles involved and to illustrate how these have been applied in the different branches of these fields of activity.

In general there are two ways in which radioactive isotopes are being used: as discrete sources and in tracer applications. In the first place radioactive substances emit alpha, beta, gamma and x-radiations, and when these radiations fall on matter they are absorbed and scattered to an extent which is characteristic of the material, and the type and energy of the incident radiation. These complex processes are being increasingly employed in gamma radiography, thickness and density gauges, empty packet detectors and level gauges, in all branches of engineering and allied research.

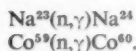
Since the chemical behaviour of radioactive isotopes is practically identical with that of their stable counterparts, they can be used, when uniformly mixed with stable material, as indicators or tracers of the presence of a particular element or compound. The radiations emitted, and hence the presence of the isotope itself, can usually be determined at different points in a system into which the isotope has been inserted, so that the dynamic characteristics of such systems can be determined. This method of employing radioisotopes has been widely used for researches on a laboratory scale as well as in industrial processes.

The many radioisotopes which can now be produced have properties which vary greatly from one to another. The conditions of use, and the way in which a particular problem is to be approached, depend very greatly on these different characteristics. It is therefore desirable to examine them briefly in order to be able to appreciate the advantages and limitations of each.

Production and Properties of Radioisotopes

Radioisotopes are atomic species whose nuclei contain the same number of protons but different numbers of neutrons. Thus, since the number of protons determines the number of extra-nuclear electrons, their chemical properties are identical (with some minor exceptions) but their atomic weights are different. Many elements have several naturally occurring isotopes: tin, for example, has ten. Some, like sodium, have only one.

Using different types of nuclear bombardment, the stable arrangements in atomic nuclei can be disturbed so as to leave too many or too few neutrons for stability. Radioactive isotopes are thus formed. Their nuclei revert to more stable forms by the emission of radiation. The most efficient way of producing radioisotopes is by neutron irradiation of a suitable stable isotope in a reactor. Neutron capture, followed by release of excess energy in the form of prompt gamma radiation, produces isotopes of the target element. Thus,



An alternative, though much less frequent reaction, may occur: a neutron is captured and a proton is emitted. Thus,



In this type of reaction a new element is formed which may be chemically separated from the parent stable substance. In addition to the production of isotopes by nuclear bombardment, a fairly wide range are available as separated fission products from the fuel rods of nuclear reactors. Some examples are: Kr^{85} , Sr^{90} , Cs^{137} , Ba^{140} , and Ce^{144} .

The nuclei of radioactive isotopes produced in these ways return to stability (disintegrate) by the emission of beta particles and gamma rays. The disintegration rate of a radioactive source is mea-

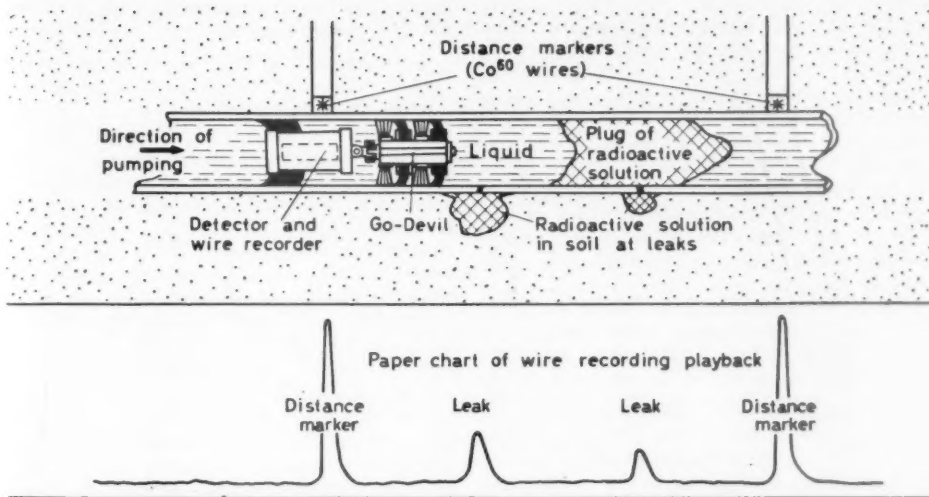


Figure 1. Internal method of leak detection for large diameter pipes—A finite volume of radioactive solution is pumped along the pipe and penetrates the pipe wall permeating the soil around the position of the leak. The radioactive solution is followed by a Go-Devil and wire recorder which is played back at the end of the run. The trace is calibrated by radioactive markers of low strength

sured in curies: one curie is defined as 3.7×10^{10} disintegrations per second and is approximately the disintegration rate of one gram of radium which was the original basis of the unit.

The radiations which are emitted are random in time and direction, but the mean rate—the disintegration rate—is proportional to the number of radioactive nuclei remaining, and can therefore be shown to decay exponentially with time. The half life of a radioactive isotope is defined as the period required to halve the initial disintegration rate. For practical purposes isotopes are used with half lives which vary from a few hours to a few years. When choosing an isotope for a particular purpose the general rule is to use the shortest half life compatible with the duration of the investigation.

Another important characteristic of a radioisotope is its specific activity, which is defined as the number of curies per gram of the element. The equation governing the rise of specific activity in a reactor is given by,

$$S = \frac{0.6\phi\sigma}{3.7 \times 10^{10}A} [1 - \exp(-0.69t/T)]$$

where S is the specific activity of the product in curies per gram, ϕ the neutron flux in $n/cm^2/sec$, σ the excitation cross section in barns (one barn equals $10^{-24}cm^2$). A is the atomic weight of the bombarded element, t the irradiation time in the reactor, and T is the half life of the isotope.

The excitation cross section (or probability of a nuclear reaction occurring) varies from element to element and is the main factor which determines the maximum specific activity which can be achieved. Iron has a particularly low excitation cross section and hence can only be produced with a low specific activity. If higher specific activity iron were available, then a greater range of experiments could be contemplated. This may be possible when higher flux reactors are in operation.

Radiations and their Detection

The main radiations with which we will be concerned are gamma rays, beta particles and alpha particles. Generally, gamma rays follow the emission of beta particles, but some pure beta emitters exist. The most important of these are: H^3 , P^{32} , S^{35} , Ca^{45} , Sr^{89} , Sr^{90} , Y^{90} , Pm^{147} , Tl^{204} . These isotopes are important in thickness gauges, static eliminators and in some tracer experiments.

Beta particles and gamma radiation are detected either by ionization chambers, Geiger counters or scintillation counters. The ionization chamber is not in general used to record individual pulses, but to measure the total ionization current. It is used in conjunction with relatively high intensity sources and has its most important application in radiation thickness gauges.

Geiger counters record individual events and are almost 100 per cent efficient for beta particles which traverse the counter but are seldom greater than one per cent efficient for gamma rays. With counting rates above 500 per second the Geiger counter rapidly becomes non-linear, and hence is limited to low intensity measurements. The associated electronics are, however, simple, and with the above reservations the Geiger counter has important application in the fields under discussion. Much higher gamma ray detection efficiencies can be obtained if scintillation counters are used. In addition the resolving time is of the order of one micro-second so that higher radiation intensities can be measured. The scintillation counter has been a useful laboratory instrument for many years and it is now finding increasing application in more arduous environments.

Although the above instruments can be designed to measure alpha particles, a frequent method used to detect this radiation is the photographic film. In special cases it is used as a detector of high sensitivity, but its most useful application is in investigations into the distribution of one radioactive substance inside, or on the surface of, another non-radioactive substance. In general radioactive areas separated by 50 to 100 microns can be resolved, and under optimum conditions resolution can be as low as 10 microns. This technique, known as autoradiography, is essentially very simple, and involves applying a photographic emulsion to a smooth surface of a section of the specimen containing the radioisotope. The emulsion is hardly sensitive to gamma rays, because of the low stopping power of such a film, but is highly sensitive to beta and alpha particles. Using this technique important studies have been made of diffusion rates, impurities and inclusions, and wear and surface porosity.

Accuracy and Statistics

The speed and accuracy of radioactive measurements are largely determined by the statistical fluctuations in the detector output caused by the random nature of the disintegration process. The accuracy of an observation is usually quoted in terms of the standard deviation of the number of counts n recorded, and as the fluctuations follow a Poisson distribution, this is given by the square root of the total number of counts, \sqrt{n} . The relative standard deviation is the reciprocal of this number, $1/\sqrt{n}$. Thus, if a relative standard deviation of one per cent is required, it is necessary to record a total of 10^4 counts. If one second is allowed for the measurement, then it is necessary for the detector to operate at 10^4 per second. If, however, the detector is operating into a counting rate meter with a time constant RC , then the relative

standard deviation in the result is $1/\sqrt{(2nRC)}$, where n is the average counting rate.

In experiments of this type it is theoretically possible to improve the accuracy by increasing the amount of radioisotope used, though limitations are imposed by the final level of activity which may appear in the product, the health hazard, and the specific activity of the injected isotope. The last mentioned can limit the information obtainable from the study of flow patterns, for instance, when external radiation detectors are being used, and it is undesirable to modify steady state conditions by the insertion of a large volume of material. The shorter the time available for observation the greater the importance of having a high specific activity. On the other hand, if radioactive samples can be removed for assay in the laboratory, the specific activity of the parent solution is usually less of a limitation and an accuracy of one per cent, or less, should be obtainable, even when the counting rate due to the sample is only of the order of the natural background of the counter.

Some Applications: Leak Detection

In civil engineering the use of radioactive tracers provides an important means of detecting leaks in pipes carrying both liquids and gases. Most exhaustive tests have, however, been made on liquid systems, especially on water mains. A number of methods of leak detection have been evolved¹.

Static Method of Leak Detection—In this method the pipe under test is filled with a solution containing a gamma emitting isotope— Na^{24} is usually employed but it is not the only possible isotope—and pumped up to pressure so that the radioactive solution is forced out through the pipe wall into the containing earth. The radioactive solution is then cleared from the length of pipe and the only active solution is then outside the pipe and concentrated around the positions of leak. The leak can be located by one of the three following methods:

(i) by lowering a detector in turn down each of a series of vertical holes from the surface to the level of the pipe;

(ii) by pulling a radiation detector along the inside of the empty pipe. If the detector is attached to a marker wire, and connected by cables to a counting rate meter at one end of the pipe, it is a simple matter for an observer to establish the position of a leak through a rise in the counting rate as the detector passes the active deposit;

(iii) using the method described by J. F. CAMERON and S. JEFFERSON² in which a radioactive solution is pumped along the pipe so as to pene-

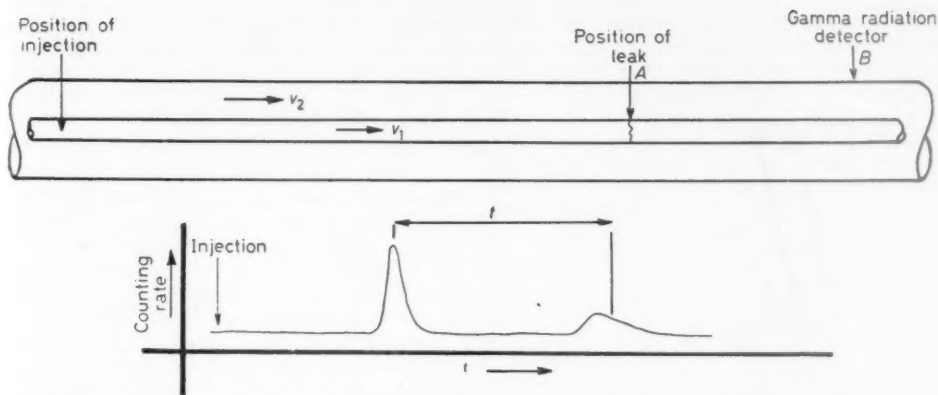


Figure 2. Concentric pipe system for leak location and typical trace—the distance AB from the leak to the detector is given by $v_1 v_2 / (v_1 - v_2) \cdot t$ where v_1 and v_2 are the velocities in the inner and outer sections of the pipe respectively and t is the time between the centroids of the recorded pulses

trate leaks as it passes. It is immediately followed by pure water to flush the inside of the pipe and then at a suitable distance by a Go-Devil towing a battery operated detector. The detector contains Geiger counters, and a miniature wire recorder, into which the output pulses of the Geiger counters are fed. A wire record is thus obtained of the distribution of radioactivity along the length of pipeline: in particular the activity of the soil at leaky points is recorded, together with that of small Co^{60} wires placed at intervals along the pipe to serve as distance markers (see Figure 1).

Flow Velocity Method of Leak Detection—Large leaks can be traced to their origin by measuring the flow velocity in a pipe closed at one end and fed with water from the other, provided that the flow through the leak is sufficient to ensure turbulent conditions in the pipe. In the method described by S. JEFFERSON *et al.*¹ a small volume of radioisotope is injected into the input flow and measurements made of the transit times of the active pulses between a series of accurately positioned detectors. The location of a leak between two adjacent detectors corresponds to an increase in transit time in that section.

Leak Detection in a Concentric System—An interesting problem in leak detection and location occurs in a concentric pipe system when the contents of one of the pipes leaks into the other. Provided that the flow velocities in the two pipes are known, and are turbulent and different, the position of the leak can usually be established. One method² involves injecting a short radioactive pulse at one end of the system and having a radiation detector at the other. When a leak is present

the detector will record two pulses, one due to the radioisotope flowing in the pipe into which the injection was made, and a second due to the radioactive fluid which has leaked into the adjacent pipe and is moving at a different velocity (see Figure 2).

It is difficult to generalize as to the positional accuracy obtainable with this method, or to specify the smallest leak which can be located, as accuracy depends on the length of the system, the pressure difference between the two flows, and the Reynold's numbers. In some practical systems, positional accuracy of a few per cent over a distance of about 100 yards is possible for leak rates of 0.1 per cent. With larger systems the accuracies will be reduced.

Identification of Go-Devils

When long pipelines are first constructed it is common practice to clean them of debris by passing a hydraulically propelled scraper known as a Go-Devil through the pipe. This device, which is driven forward under pressure from one end, occasionally fouls and stops. Under such circumstances it is obviously a great help to know its precise location so that the obstruction can be removed with minimum effort. One satisfactory method of marking the Go-Devil is to incorporate a radioactive source which can easily be found by walking alongside the pipe with a radiation detector. For exposed pipes one microcurie of Co^{60} is sufficient, and with 500 microcuries Go-Devils in pipes buried in four feet of earth can be detected.

To overcome any radiation hazard to operators during loading and recovery, the source is normally housed in a lead shield from which it is released only by the driving pressure supplied from one end

of the pipe. In this way the source is completely screened when the Go-Devil is to be approached but can be exposed when required for detection underground.

Gamma Radiography

The use of x-radiography for the examination of welds, castings, forgings and other objects is now well established. X-ray machines operating at potentials from one hundred to several thousand kilovolts are in routine use for flaw detection in structures ranging from light alloys to steel components up to ten inches thick. Gamma rays from small intense sources of radioisotopes can also be used for similar purposes. We will briefly examine the essential features of each technique.

The penetrating power of x-rays from an x-ray machine depends on the magnitude of the potential difference maintained between anode and cathode of the tube, and in any given installation it is usually possible to vary the voltage over a significant range so that x-rays with greater or less penetration are available from the same machine. The x-rays generated form a continuous spectrum with a maximum energy corresponding to the applied voltage: the maximum intensity corresponds to a voltage which is approximately one third of the maximum.

In contrast, radioisotopes emit gamma rays with discrete energies which range from a few thousand electron-volts to several million electron-volts for different isotopes. For example, Cs^{137} emits gamma rays of a single energy of 0.667 MeV; Co^{60} has two gamma rays with energies of 1.17 and 1.33 MeV for each disintegration of the

nucleus: Tm^{170} emits weak gamma radiation with an energy of 0.084 MeV and is used to examine thicknesses in the range 0.05 in. to 0.3 in. steel. To cover the range of thicknesses required by industry a number of different isotope sources are required and the most useful are listed in Table 1.

When not in use a gamma ray source is enclosed in a lead container to avoid all radiation hazard. In spite of its weight this container is lighter, less fragile and more easily handled than an x-ray set with its ancillary apparatus. The gamma ray source is removed from its container by a simple remote control and because of its small size is especially convenient for radiographing objects from the inside. An important example of this type is the radiography of a circumferential pipe weld which can be done with a single central source and a film wrapped round the pipe. The portable nature of the source, and the fact that neither cooling nor power supplies are required, means that the source may be rapidly moved from one site to another and radiographs obtained on fixed assemblies in remote locations.

The intensity of the radiation emitted by gamma ray sources is significantly less than that emitted by x-ray machines. An exposure of one minute by a machine would be equivalent to an exposure of several hours by an isotope source of the activity normally used. To a large extent this can be overcome by arranging to radiograph a number of objects at the same time; a technique which is possible since the radiation from a single source is isotropic.

Sources supplied by Harwell are in the form of cylinders, and vary in size from 1×1 mm to 6×6 mm

Table 1. Some properties of radioisotopes commonly used in gamma radiography

Radioisotope	Maximum specific activity (mc/g at P.F.1)	Half life (years)	Gamma radiation energies (MeV)	Useful thickness range	
				in steel (cm)	in light alloys (cm)
Cobalt 60	990	5.25	1.17 1.33	3-15	—
Caesium 137	4 c/g max. fission product	30.0	0.667	2-7	3-12.5
Iridium 192	3200	0.204	0.296 0.308 0.316 0.468 0.484 0.604 0.613	1.5-6.5	2.5-10
Thulium 170	1250	0.348	0.084	0.1-1.0	0.5-2.5

diameter and length, whereas the focal spot of an x-ray tube can have dimensions less than one millimetre diameter. The larger isotope sources thus produce a penumbra which diminishes the definition in the radiographic image. The smaller

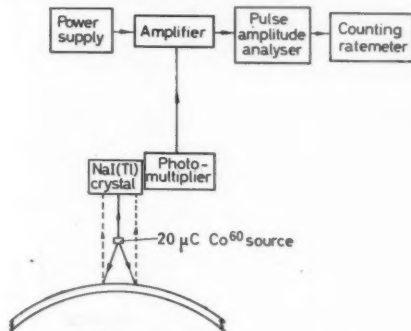


Figure 3. Schematic diagram illustrating the principles of the Tube Wall Thickness Gauge

sources correspond to lower gamma ray intensities, but when these can be used the resolution is comparable with that from an x-ray machine. If nuclear reactors with very high neutron fluxes become available for isotope production, gamma ray sources of higher intensity and smaller size will become available.

From these considerations it should be clear that the two techniques are complementary, and in a broad approach to flaw detection problems they should both be considered on technical and economic grounds together with other possible methods such as ultrasonic, magnetic and chemical techniques.

Thickness Gauges and Allied Applications

A wide variety of instruments using radioactive isotopes are now available for the testing and control of engineering products. Included in this class are such instruments as beta and gamma transmissions and scattering gauges, gas and vapour analysis and impurity gauges.

Beta ray thickness gauges are used to measure thin materials such as paper, plastic, metal foils, tobacco, rubber and linoleum. A typical application of beta gauging⁴ is in the measurement of cold rolled strip in the thickness range from 0.005 in. to 0.05 in. steel or 0.005 in. to 0.15 in. aluminium. The instrument described uses 50 mc of Sr^{90} plus Y^{90} as the source and air filled ionization chambers as the detectors. The accuracy is claimed to be ± 0.00005 in. with an integrating time of 0.05 sec; the drift is said not to exceed 0.00002 in. per week.

A beta ray gauge is in use in the tin-plate industry to sort steel sheet according to the total mass per unit area. In conjunction with a variable memory storage device, sheets travelling at 300 ft/min and differing at any point of their length by more than one per cent of the total mass per unit area can be rejected. It is intended to develop the instrument so that it will sort sheets travelling at 2000 ft per minute.

A gamma ray thickness gauge used for measuring hot rolled steel strip in the range 0.05 in. to 0.30 in. has been described by G. SYKE⁵. A 500 mc source of Tm^{170} is employed with a water cooled scintillation counter using sodium iodide as phosphor. With an integrating time of 1.6 sec an accuracy of 0.4 per cent is obtained. This instrument has also been designed to measure the wall thickness and eccentricity of red hot steel tubes with diameters of 2 in. to 6 in. and wall thicknesses of 0.1 in. and 0.6 in.

The principle of gamma ray absorption has also been employed to detect empty or underfilled packages on a conveyor. The method is becoming increasingly popular since no access to the inside of the container is required. An example of this class of application is that in which the level of coke and ore has been controlled in a hopper feeding a zinc smelting furnace.

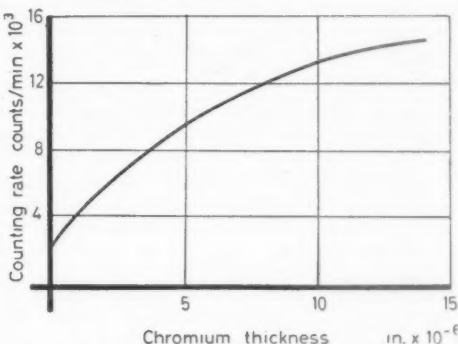


Figure 4. Increasing intensity of x-rays from chromium plate deposited on 0.01 in. thick nickel backing foil. The exciting radiation is Bremsstrahlung from a tritium source of approximately 100 mc

For measuring the wall thickness of tanks or pipes, where only the outer surface is accessible the intensity of back-scattered gamma rays is used⁶. The principle of the instrument is illustrated in Figure 3 and its operation depends upon the following factors.

(i) The height of the output pulse from a sodium iodide scintillation counter is proportional to the energy of the incident radiation;

(ii) The energy of the secondary radiation scattered back from the wall to the detector is lower than the energy of the primary radiation; and

(iii) It is possible to discriminate electronically between the amplitudes of the output pulses from the detector corresponding to the primary and scattered radiations.

The counting rate corresponding to the back-scattered radiations increases with the wall thickness up to a saturation value at about one inch of steel. In the instrument described a source of only 20 μC of Co^{60} is required, and the accuracy is about four per cent from 0.1 in. to 0.75 in. steel with an integrating time of ten seconds.

There has recently been a considerable revival of interest in the technique of x-ray fluorescence spectroscopy which is the name given to the method of analysis in which elements are recognized by the excitation and measurement of their characteristic x-ray spectra. In a recent paper, G. B. COOK *et al.*⁷ have described an apparatus for x-ray fluorescence spectroscopy using a radioactive source to replace the x-ray tube, and an electronic counter, capable of discriminating between x-rays of different energies, to replace the crystal spectrometer. This arrangement, although not as sensitive as the crystal spectrometer, has the virtue of being simple and cheap, and comprises a very useful instrument when the full performance of the more complex unit is not required.

Although still under development, especially from the point of view of determining the most suitable sources, the following results give an indication of its performance. Using an H^2 Bremsstrahlung source of 100 mc measurements of chromium plate on a nickel backing foil of 0.01 in. thickness gave approximately 100 per cent increase in background counting rate for a chromium layer of 1×10^{-6} in., and 400 per cent for a layer of 4×10^{-6} in. Details are given in Figure 4. The thickness of cadmium on iron can be measured by this apparatus using an W^{181} source by direct excitation of the cadmium K -x-ray. Cadmium plating from 10^{-5} in. to approximately 5×10^{-3} in. can be determined to within an accuracy of five per cent.

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Essay

Competition

for Schools and Technical Colleges

This year TECHNOLOGY has joined RESEARCH in sponsoring the Competition and extending its scope to include pupils from technical colleges and secondary modern schools. Prizes of £15 will be awarded for the best entry and £10 for the next best entry in Sections I and II; prizes to the same value will also be presented to the school or college library of the prizewinners. In Section III there will be a first prize of £30 and a second prize of £20. In each case the prizes may take the form of books or instruments.

Section I

A report, about 800 words long, on any piece of practical work or project in biology, chemistry or physics written by a school student whose *sixteenth birthday falls on or after June 1st, 1959.*

Section II

A report about 1000 to 1500 words in length, on any piece of practical work or project in biology, chemistry or physics written by a school student *over the age of sixteen on June 1st, 1959.*

Section III

A critical essay of about 1000 to 1500 words on which of the 'new' metals promises to be most useful in technology. This section is open to any student attending a technical college who is *under the age of twenty-one on June 1st, 1959.*

Entries will be accepted after June 1st, 1959 and the final closing date is July 31st, 1959. Please write for full details to The Editor, RESEARCH, 4 and 5 Bell Yard, London, W.C.2.

DOCILE SEQUENCE ENGINE

A New Type of Model for a Learning Machine

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IN engineering practice, automatic controllers of processes where feedback is not employed, *e.g.*, automatic lathes are essentially hierarchic. At the apex of the hierarchy stands a data storage and reading device—camshaft and followers, magnetic tape and deck, punched card and reader, *etc.* This contains the process instructions in compact form, and these are decoded and implemented by slave devices lower in the hierarchy.

Docile Sequence Engine (D.S.E.) is a theoretical model for a mechanism which—it is believed—has not been proposed hitherto. It is a non-hierarchic process controller in which the process instructions are diffused throughout the system. It comprises a number of similar units, each of which has two states: a stable 'off' state, and a metastable 'on' state. For each unit, the 'on' state is to be thought of as initiating, modifying or terminating some part of the process controlled. Thus, activity in one unit may switch on a motor, whilst activity in another might switch it off again. Any unit may be set to the 'on' state at the will of the operator, for example by pressing a button, and in this way a process may be carried out by pressing such buttons in an appropriate sequence and with suitable time relationships.

The important feature of D.S.E. is that, after a process has been carried out manually a few times, the apparatus will 'learn' the sequence employed.

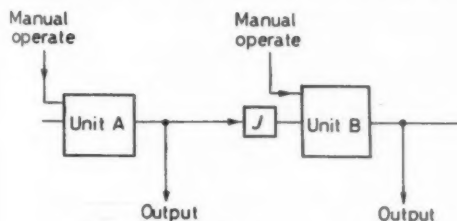


Figure 1

The sequence can then be evoked merely by the pressing of the first two or three buttons, the remainder of the process being carried out by the D.S.E. automatically.

A number of processes can be stored within D.S.E. in this manner. It will be shown that the

apparatus can be simpler if the processes are substantially different from one another. A simple D.S.E. is liable to confusion if two processes contain similar sequences, and may switch over to the

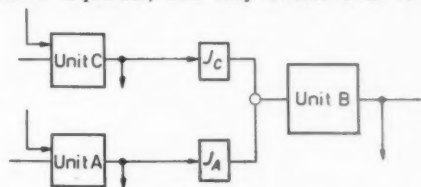


Figure 2

wrong process if this is the case. Such mistakes can be avoided in a D.S.E. of sufficient complexity but if process *A* contains a sequence similar to a sequence occurring in process *B*, the number of components required rises rapidly with the number of elements in the shared sequence.

Principle of Operation

In Figure 1, two units are shown. Unit *A* acts on unit *B* at the box labelled *J*, which will be called a 'junction'. Whenever *A* operates, it places in *J* a fixed quantity '*Q*' of something which might be electrical charge, or some chemical substance. *Q* then decays with time, so that at any subsequent instant *t* an amount *Q(t)* remains. An exponential decline,

$$Q(t) = Qe^{-kt}$$

is a suitable decay relationship. In *J*, another quantity *S* is stored. When *Q(t)* declines to the value *S*, the unit *B* operates; that is, switches over to the 'on' state for a short period, then returns to the 'off' condition. When the apparatus is first set up, *S* is zero and unit *B* only operates after an infinite time. However, suppose it is desired that unit *B* operate at a time *t*₁ after unit *A*. Then, when *t*₁ has elapsed, unit *B* is operated manually. It is arranged that whenever *B* operates, *S* → *Q(t)*₁ with some time constant *T* which is an arbitrary parameter for the whole system. If such a training procedure be repeated a few times, *S* will approach indefinitely near to *Q(t)*₁ and eventually *B* will operate at time *t*₁ without manual intervention.

This is the principle of D.S.E., and may clearly be elaborated in several ways. A trivial extension is to

arrange that unit *B* operates another unit, *C*, after a further period t_2 . An open string of units assembled in this way can control a process in which events occur in a fixed order, but in which the times spent in successive states may be determined by the operator.

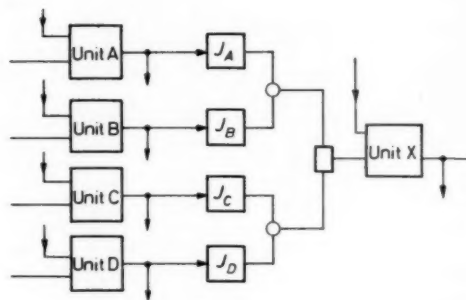


Figure 3

Evidently there will be occasions when we require unit *B* to operate only if unit *A* has operated (at some time earlier by an amount t_A) and if unit *C* has also operated (at some time earlier by an amount t_C). We achieve this with the arrangement in Figure 2 where the sign ϕ represents a logical 'and'. As a result of training, the quantity S_C in J_C approaches $Q(t_C)$; similarly S_A in J_A approaches $Q(t_A)$. Thereafter, unit *B* will only operate when the conditions that $Q_C = Q(t_C)$ and $Q_A = Q(t_A)$ are satisfied simultaneously. This is the required condition.

By having logical 'and' units with more than two inputs, say m , we can arrange that unit *B* only operates when m other units have operated according to some desired history. If there are n units, and each has junctions with all the others, including itself, then $m = n$ and the D.S.E. may be said to be 'fully interconnected'. There will be n^2 junctions, and the condition for a unit to operate is uniquely determined by history of the whole of the rest of the system. Full interconnection would in general be unnecessary, and frequently undesirable. For example, in driving a car, the situation in which the horn should be blown is not a function of the amount of petrol in the tank.

D.S.E.'s of the Figure 2 type allow each unit to take part in only one sequence. Of the large number of possible operating sequences, only one can be stored involving all n units, though of course two may be stored involving $\frac{1}{2}n$ mutually exclusive units, four involving $\frac{1}{4}n$ units, and so on. D.S.E.'s in which each unit can take part in only one (or no) sequences may be called first order.

Higher Order D.S.E.'s

In D.S.E.'s of order ' p ' a unit can take part in p different sequences. For example, in Figure 3, the sign ϕ represents a logical 'or'. Unit *X* operates whenever *A* and *B* have operated at the required time before, or whenever *C* and *D* have operated at the required time before. In this case p is two; higher order units have 'or' boxes having the appropriate number of inputs. With D.S.E.'s of second order and above, a difficulty arises. If *X* has been trained to operate after *A* and *B*, so that S_A has some value Q_{A1} and S_B some value Q_{B1} , then on training *X* to operate after *C* and *D*, the quantities S_A and S_B will be lost, since Q_A and Q_B will in general have new values Q_{A2} and Q_{B2} , and when *X* is operated, S_A and S_B will approach these.

One solution to the difficulty, not ideal, is to assume that when *X* is required to operate after *C* and *D*, the quantities Q_A and Q_B will probably have decayed to a low value. Certainly they will have done so if there is a convention in training that no unit shall be required to take part in two different sequences at instants too close together in time. If this is an acceptable restriction, then a reasonable additional rule is that at the i th junction J_i , the learning (and therefore lesson-forgetting) time constant T_i shall be a function of $Q(t_i)$ such that T_i is short when $Q(t_i)$ is large, and very long when $Q(t_i)$ is small.

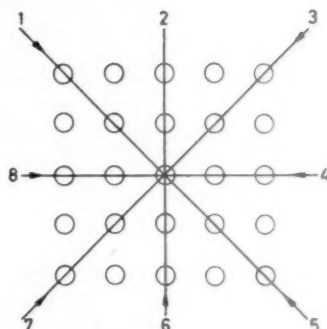


Figure 4.

In a D.S.E. where n equals 16, say, the number of sequences involving all the units once, and assuming all the intervals between operations to be equal, is $16!$, which exceeds 10^{13} . The number of possible sequences, using any number of units up to 16, including some of them twice, and with freedom to choose intervals, is of course many orders greater. Evidently a fully connected D.S.E. able to store an appreciable fraction of the whole range of possible patterns is beyond the bounds of the practicable, for

we should have $m = 16$, $n = 16$, $p > 10^{13}$, and the number of junctions required is the product of these numbers.

Nevertheless, by restricting the types of sequence the machine has to handle, it is possible to bring p down to less than 100. For example, suppose the units be arranged in an array (Figure 4) and suppose the restriction is that units which are close together in space operate close together in time. If regions in the array control stages in the process, such a restriction is probably not too onerous, and excitation of the units will occur in a wavelike manner.

To determine when a unit shall operate, it would often be sufficient to have it measure the state of its neighbours, and the state of the neighbours of those neighbours. That is, m equals two. The excitation wave may be expected to reach the unit from any of eight directions, and may have reached the preceding unit also from any of eight directions, yielding p equal to 64. If n is 16, we find 1028 for the number of junctions; in fact the number is not as great as this, because units at the boundary of the array do not have so many neighbours.

Such a D.S.E. can successfully distinguish, learn, and repeat the processes presented by Figure 5, because only one unit is common to the two processes. The sequences represented by Figure 6 can also be distinguished, retained and reproduced provided the duration of the single transition shared by the two sequences are different. If these durations are similar the subsequent transition will not be uniquely defined and the machine may switch to the wrong sequence. To be quite certain this will not arise one needs $m=3$, $p=512$, requiring a much larger number of junctions. Similar remarks then apply to sequences containing two shared transitions.

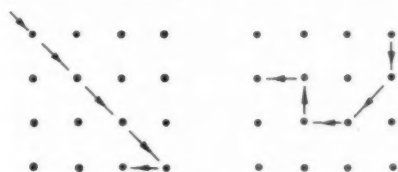


Figure 5

Discussion

The high rate at which the number of junctions has to be increased with discriminating power over similar sequences probably excludes D.S.E. from the range of economic engineering propositions. Nevertheless, there may be some profit in building a small one, and a machine having $n = 3$, $m = 2$, $p = 2$ is at present under construction in this laboratory. Systems which grow by pushing out

tree-like formations rapidly acquire a large number of peripheral structures which can make junctions with other, similar systems, and the animal neuron is an example. D.S.E. is put forward tentatively as a pos-



Figure 6

sible model for motor regions in the central nervous system. Such models have been proposed by a number of authors (for example refs. 1-10) and some of these^{1,2}, consider the central nervous system in a rather general way, discussing factors affecting its growth and stability. Most are concerned with the interpretation of input data³⁻⁸, or with the efficient transmission thereof⁹; the models adduced are therefore presumably of sensory parts of the central nervous system. Process controllers which learn have been considered¹⁰, but which learn in the sense defined by W. H. THORPE¹¹ and interpreted by A. M. ANDREW as associated with goal-seeking behaviour.

Such learning is of a more sophisticated kind than that exhibited by D.S.E., and corresponds to improvements in the performance of the operator of D.S.E., rather than of D.S.E. itself. The motor sequences generated by D.S.E. can result from a distribution of S values initially ('genetically') imposed, or can be 'habits' ('reflexes') achieved as a result of training under an operator, either human, or a mechanism of the type Andrew has considered. In the latter role, D.S.E. may be regarded as a repository for the motor solutions to problems in control already solved, freeing the operator for the solution of new problems.

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RESEARCH

The 1959 Waverley Gold Medal Essay Competition

RESEARCH is this year sponsoring The Waverley Gold Medal Essay Competition for the seventh year in succession. The Competition is designed to encourage the scientist in the laboratory and the engineer in the production plant to express his views and translate his work into an essay that will readily be understood by other scientists, directors of industrial firms and others interested in science and technology.

The **Waverley Gold Medal**, named after and bearing the coat of arms of the late Lord Waverley, together with **£100** will be awarded for the best essay of about 3,000 words describing a new scientific project or practical development giving an outline of the scientific background, the experimental results and the potential application of the project or process in industry. The essays will be judged for technical content by specialists in the subject, for clarity of presentation and for style.

A second prize of **£50** will be awarded and also a special prize of **£50** for the best entry from a competitor under the age of thirty on 31st July 1959. If the first prize is awarded to a competitor under the age of thirty, the special prize will go to the next best entry. For full details write to the Editor of RESEARCH, 4/5 Bell Yard, London, W.C.2.

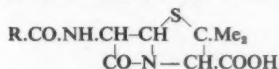
All entries must be received by the Editor not later than 31st July 1959

SURVEY

A New Range of Penicillins

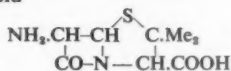
Four members of the staff of the Beecham Research Laboratories have recently published some of their work on 6-aminopenicillanic acid which can only be described as a major scientific advance. They were investigating the possibility of producing, by conventional fermentation methods, a penicillin which would be amenable to chemical modification after fermentation and might prove to be effective against organisms resistant to penicillin.

The most commonly used penicillin G is



where the side chain R is Ph.CO.NH-. The other known penicillins differ only in the nature of their side chains and, although penicillin has been made by chemical synthesis, all commercial material is produced by growing a selected organism in a broth and feeding in a precursor. The latter is then incorporated into the molecule during the microbiological synthesis.

During these experiments two methods of assay were used, microbiological and chemical, and it was found that for certain conditions the results consistently disagreed. It was thought that the brew must contain the core of the penicillin molecule, 6-aminopenicillanic acid



and when the correct side chain was added, penicillin G was produced.

The importance of the discovery is that this basic penicillin skeleton can now be used to synthesize a whole range of 'taylor-made' antibiotics in a very short time. It is expected that many of these will be non-toxic, like the basic molecule, and some should be effective against organisms such as staphylococci, which are resistant to the known penicillins, while others may be used to combat typhoid, various intestinal disorders, tuberculosis, etc. It should also be possible to produce a modified penicillin suitable for patients who are allergic to the present range.

Experiments are already being conducted on some of the new compounds both in vitro and in laboratory animals. The work has been carried out by F. R. BATCHELOR, F. P. DOYLE, J. H. C. NAYLOR and G. N. ROLINSON in consultation with Professor CHAIN, who jointly with Fleming and Florey was awarded the Nobel Prize for the penicillin discovery

in 1945. The Beecham Group are proposing to develop this discovery in partnership with one of the big American pharmaceutical companies for it was pointed out that the resources available in the United States might speed up the development process by two to three years.

Scientific and Engineering Manpower

The Chairman of the Parliamentary and Scientific Committee, Richard Fort, M.P., has published in a re-statement* of the problem of the shortage of scientific and engineering manpower. If the United Kingdom is to maintain its present rate of industrial development, higher education in science and engineering will have to expand as rapidly during the next, as it has done during the past ten years. An analysis of the present position leads to the conclusion that the United Kingdom should aim at about 20,000 graduates in pure and applied science by 1970 compared with the 10,000 graduating now.

A notable feature of our system of technical education is the different routes by which scientists and engineers can qualify at a university or at a technical college, and therefore government policy for increasing scientific and engineering manpower has included an increased university building programme and special grants to promote research work in technical colleges.

Available resources of manpower should be used to the best advantage: scientists and engineers must be correctly used by employers and not be occupied with work which could be done by less able staff; qualified personnel should be used in the most important industries and industry should reconsider its present reluctant attitude towards the employment of women graduates. More scientists in responsible administrative and commercial posts are not 'wasted' and progressive industrial managements increasingly appreciate that the application of scientific methods can result in the more economical use of workers' time and in increased productivity.

The source of future scientific and engineering manpower lies with the boys and girls currently following an academic programme and therefore pupils who are undecided whether they prefer science or the arts should be encouraged to take science. This trend could be aided by allowing the student to master enough mathematics to prevent him from being discouraged by the sciences. The universities, on the other hand, should revise their standards to

* FORT, R. *Scientific and Engineering Manpower Survey*. Published by P.E.P. (January, 1959). Price: 2s 6d

make it possible for the schools to strike a balance between giving a broadly based education and encouraging the undecided to take science.

The most serious aspect of the manpower situation is the shortage of science teachers, which affects



Figure 1. Varian electromagnet with 12 in. pole faces as recently installed at the Electronics Department, Southampton University. The magnet weighs 3 tons and had to be lowered through the roof into the new building. (By courtesy of Varian Associates, U.S.A.)

both the schools and the technical colleges and Mr Fort claims that the government has tried to remedy this by increasing teachers salaries. (The salary scales are still heavily weighted in favour of industry). The author concludes that 'attracting more pupils to take science first in the schools and then in the universities, and improving the teaching of mathematics would probably be the two most promising steps for providing more science teachers in schools. This after all is the whole problem of training more scientific and engineering manpower'.

Is Mr Fort sure that the manpower is there to be trained?

Large Magnet at Southampton University

A very large electromagnet has just been installed in the Electronics Department, Southampton University to assist in the research work of the microwave group. This magnet will be used for studies in nuclear and electron resonance, and

double resonance experiments in which both the nuclear and electron spins are turned over simultaneously.

As the work on these new techniques of magnetic resonance has progressed the need for more and more homogeneous magnetic fields has arisen. This is because the second and third order interactions between the atoms and nuclei produce fine splittings of the absorption which can only be resolved if the inhomogeneity of the magnetic field is considerably less than the spectral splitting. Some of the line splittings are only of milligauss order and since the applied field is about 10,000 gauss, homogeneities of at least 1 in 10^7 must be available over the specimen volume. The production of such high degrees of uniformity is a major task in precision engineering, and magnets with pole face diameters of up to twelve inches are required. The installation of this magnet at Southampton will thus increase the available resolving power in their microwave and radiofrequency spectroscopy by several orders of magnitude.

Current problems of investigation include the effects of irradiation damage, and the role of free radicals in different physical and chemical systems.

The magnet is actually a Varian 12 in. diameter electromagnet (see Figure 1) of three tons weight, and £6,000 cost—the money for which was provided by a special grant from D.S.I.R. D.J.E.I.

Research at the Alkali Division

The research laboratories of the Alkali Division at Winnington, near the site where Brunner and Mond started their original works, have recently been extended by a new wing costing about £250,000; this was opened by Sir CYRIL HINSHELWOOD on March 4th.

Polythene, now being produced by the Plastics Division, was developed by the Alkali Division and a great deal of the new speculative research is devoted to inorganic polymers. The search is for polymers stable up to about 700°C —although economic products stable at 300°C would be very welcome—and it is believed that these are most likely to be found among straight chain inorganic materials; metal isocyanates such as chromyl and uranyl isocyanates are promising and other possibilities are organic phosphorus compounds.

Magnetic oxides of iron and nickel are also being investigated both from the point of view of new manufacturing techniques and possible new compositions for permanent and for soft magnets such as ferrites. Fluorine compounds are also being studied but little information was disclosed on either of the last two lines of investigation.

BOOK REVIEWS

Fast Reactions in Solids

F. P. BOWDEN and A. D. YOFFE
(ix + 163 pp; 10 in. by 6 in.)

London: Butterworths Scientific Publications.
New York: Academic. 40s, \$7.00

IN an earlier book, *The Initiation and Growth of Explosion in Liquids and Solids* (1952), the authors described their experimental work on the initiation of explosive decomposition; the present monograph is a report of progress made in this field during the ensuing six years and deals mainly with the initiation of explosion in crystals by heat, light, shock or nuclear radiation. Although concerned with fast reactions, an understanding of the mechanism of the slow decomposition of solids is important in elucidating the details of explosive decomposition; the first chapter therefore deals with recent work in which the classical measurements of gas pressure against time have been supplemented by studies using electron and x-ray diffraction, and the electron microscope to follow the progress of reaction. These have shown, for example, the mechanical break-up of crystals undergoing slow decomposition, and the development of silver nuclei in the decomposition of silver azide.

The growth of a slow reaction into an explosion may be related to the rise in temperature of the system and the consequent increase in reaction rate. If the surface area/volume ratio is too large, heat losses from the surface prevent explosion—there is a critical size below which an explosive decomposition cannot develop. These ideas were first worked out for gas mixtures in vessels, and later extended to solid explosives. Experimental data to test the validity of the theory are becoming more numerous, and the recurrent theme throughout this book is the need for the 'hot-spot', from which an explosion can develop, to achieve a critical size which seems to be in the region 10^{-5} to 10^{-3} cm. The chapters on initiation by heat, light and shock are set against this background and provide details of recent experimental work in which a wide range of experimental techniques have been brought to bear on the problem. The same concept is used to explain the somewhat surprising failure to initiate explosives (except nitrogen iodide) by nuclear radiations even at high intensities: decomposition of a few molecules along the path of a high energy particle cannot give a large enough localized hot-spot. It is anticipated that this may only be possible with beams of such high density that particle tracks can intersect and so produce larger decomposition nuclei.

The probability of initiation is also a function of the structure and electronic properties of the solid. An attempt to correlate these factors is made for metal azides. The most important factor seems to be the ionization potential of the metal—the higher its value the lower the energy required to raise the electron of the azide ion to the conduction band, a process which is postulated as the first step in the decomposition of inorganic azides by heat or light.

The spontaneous explosion of some solids has not yet been satisfactorily explained. Lead azides and mercuric

azide sometimes explode during crystallization, while exposure of a fresh surface of nitrogen iodide by removal of absorbed ammonia also leads to explosion. These and related experimental facts are surveyed in the penultimate chapter. The final chapter deals with recent work on the development of the explosion from the nucleus of decomposition. Much of this work depends on the use of high-speed photography and some beautiful examples of this technique are reproduced.

This book is to be recommended as a valuable survey of recent developments in the field of fast reactions in solids. It is clearly intended as an interim report rather than as a definitive survey, and this is reflected in the rather staccato style and the inclusion of some sections which read like a list of brief and not always logically linked abstracts. The coverage is in general wide and much of the work described is hitherto unpublished. As is to be expected in a book of this type, most of the detailed description of experimental work refers to researches carried out in the authors' group of workers and this adds a sense of vitality to the whole book.

D. H. EVERETT

Gmelins Handbuch der anorganischen Chemie (8th Edn): Silicon (Vol. 15, Part C); Oxygen (Vol. 3, Part 3) and Fluorine (Vol. 5)

(501 pp, 238 pp and 258 pp; 10 in. by 7 in.)

Weinheim: Verlag Chemie. D.M. 276, 283 and 145

SEARCHING the literature to find published information on any particular subject is a tedious operation. It is usually best left to the information officer or trained librarian, but volumes of collected references, such as the *Gmelins Handbuch der anorganischen Chemie*, can often shorten the task or may in certain cases provide all the required references at one glance.

Part C of section 15 deals with the organo-silicon compounds. (Part A, the occurrence of silicon, has not yet been published and Part B, elementary silicon and silicon compounds, is still in the course of preparation.) The covalent compounds of silicon are of particular interest at this time as they have already formed a basis of one industry, the silicone industry, and they are being intensively investigated to ascertain the analogy between them and the organic compounds of carbon; there is also the possibility of producing tailor-made silicon polymers of commercial value. The major part of the volume is devoted to the preparation of the properties of silicon, hydrocarbon compounds and the chemistry of silicones; the last includes special manufacturing problems, applications of silicone oils, resins, etc and the use of silicone rubber. All the German headings and sub-headings are also printed in English at the bottom of each page in the text. The references cover the relevant literature up to the end of 1953; a few later references only are included.

Part 3 of the section on oxygen gives all the literature references relating to elementary oxygen up to the end of 1949. It deals with the preparation of oxygen in the

laboratory including the separation and enrichment of oxygen isotopes; the physical properties of the oxygen atom, the O^{2-} ion and the O_2 molecule; magnetic and electrical properties; and the reaction of hydrogen with both pure oxygen and air. In the case of the combustion hydrogen in oxygen or air the photochemical, surface and thermal reactions in both explosive and continuous systems are covered. Data is given on flame temperature, flame velocity and ignition temperature.

The supplementary volume on fluorine covers the additional literature published during the period 1926 to the end of 1949. It gives references on the occurrence of fluorine, its preparation, physical properties, chemical

reactions and the special analytical techniques that are available for the determination of fluorine. Almost 100 of the 258 pages are devoted to the compounds of fluorine with hydrogen (78 pages), oxygen and nitrogen.

It is much to be regretted that the volumes are not more up-to-date when published for the value of these and the other volumes of *Gmelins Handbuch* is in reducing the time taken to find the required literature. The price of the individual parts, in the region of £20 to £30, means that only the wealthiest libraries can indulge in the luxury of complete sets while others will only be able to purchase the volumes of direct interest to the research workers in their own laboratories. E.S.

LETTER TO THE EDITOR

Ageing of Active Titanium Dioxide

SIR,

Although the formation and sintering of active solids has been the subject of considerable research in recent years¹, relatively little attention has been paid to deactivation—as measured by loss of specific surface—of materials at, or only slightly above, room temperature. Indeed, one might expect little deactivation to occur, since the only mechanism of loss of surface possible at these temperatures will, in nearly all cases², be one of adhesion.

However, under certain circumstances very considerable changes can occur when an active solid is raised only a little above room temperature, as was shown in the following experiment. A very active sample of hydrous titanium dioxide, prepared by hydrolysis of *n*-butyl titanate with pure water, was stored in an open tube maintained at $50.0 \pm 1.0^\circ\text{C}$ by an air thermostat; samples were withdrawn after various periods and the specific surface determined gravimetrically by nitrogen adsorption and B.E.T. procedure³. The samples were outgassed at 80°C until the rate of loss of volatile matter had fallen to less than one milligram per gram per hour and a vacuum of better than 10^{-3} mm mercury was obtained (three to four hours).

During the first ten days the specific surface fell sharply to less than half its original value (see Table 1), whilst little additional change took place over the next 65 days.

After some 80 days a further small reduction in specific surface was observed, coinciding with a fall in the surface coverage of adsorbed water to less than one complete monolayer—the area occupied by a molecule of physically adsorbed water is approximately 10 sq. Å. For the calculation of surface coverage it has been assumed that the weight lost on outgassing for specific surface determination is due entirely to loss of water.

Table 1. Specific surface and number of monolayers of physically adsorbed water for samples of hydrous titanium dioxide after ageing at 50°C in air

Ageing period (days)	Specific surface (sq.m/g)	Surface coverage*
0	539	2.30
10	256	—
20	237	—
47	237	—
76	242	1.07
90	225	0.70
100	225	0.42

* 1 mg of water occupies 3.3 sq.m.

since thermogravimetric analysis of the original material up to 1000°C gives no indication of other volatile matter being present.

The small increase in specific surface occurring between 47 and 76 days may be due to the slow evaporation of water which had formerly been blocking some of the finer pores, thus making a certain amount of new surface available to nitrogen molecules. However, it is possible that an apparent increase of this order might be due to inhomogeneity of the samples removed for determination of specific surface.

Yours faithfully,

M. I. POPE

Chemistry Department,
University of Exeter,
Devon

20th February 1959

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